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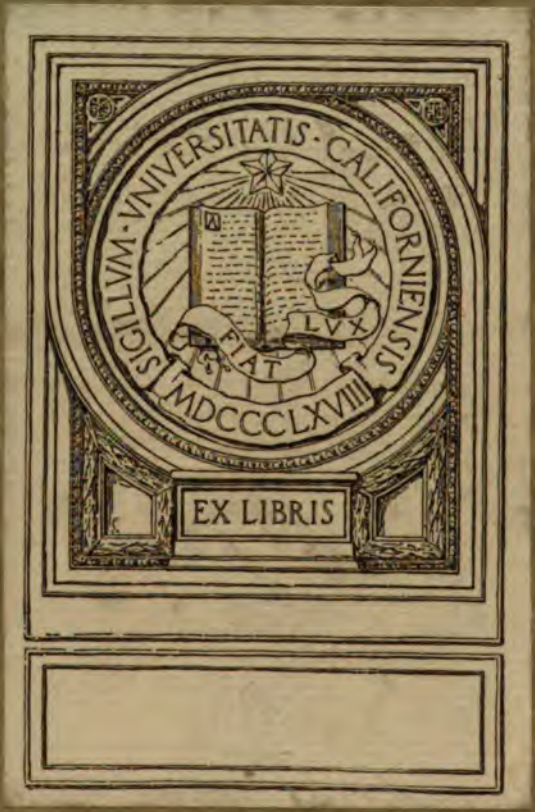

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THE METHODS

OF THE

UNITED STATES STEEL CORPORATION

FOR THE

COMMERCIAL SAMPLING AND ANALYSIS OF COAL, COKE AND BY-PRODUCTS

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CONTENTS.

	Page
PREFACE	9
SAMPLING	10
Coal Sampling	10
Sampling at Mines	10
Development Sampling	10
Sampling from Pit Wagon or Tipple Chute	12
Sampling at Works	13
Car Samples	13
Sampling as Cars Are Being Unloaded	14
Sampling Before Cars Are Unloaded	14
Belt Samples	14
Coke Sampling	15
Sampling at Mines—Bee-Hive Ovens	15
Sampling at Works—By-Product Ovens	18
Coke Plant Sample	18
Blast Furnace Sample	18
Laboratory Preparation of Sample	18
Method—Use of Laboratory Roll Machine	19
Method—Use of Diamond Steel Mortar	19
Determination of Moisture in Coal and Coke	19
Determination of True Specific Gravity of Coal and Coke	21
METHODS OF ANALYSIS	22
General Remarks	22
Proximate Analysis	22
Volatile Matter—Coal	22
Muffle Furnace Method	22
Meker Burner Method	23

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	PAGE.
METHODS OF ANALYSIS—Continued	22
PROXIMATE ANALYSIS—Continued	22
VOLATILE MATTER—COKE	24
ASH	24
FIXED CARBON	24
DETERMINATION OF METALLIC IRON DUE TO ABRASION IN COAL AND COKE	25
DETERMINATION OF SULPHUR	26
ESCHKA METHOD	26
DETERMINATION OF PHOSPHORUS	27
PREPARATORY TREATMENT OF THE SAMPLE FOR THE PRECIPITATION OF PHOSPHORUS	27
Hydrofluoric Acid Method	27
Fusion Method	28
PRECIPITATION OF PHOSPHORUS	29
FINAL DETERMINATION OF PHOSPHORUS	29
Volumetric Methods	29
Acid Alkali Titration	29
Potassium Permanganate Titration	30
Gravimetric Methods	30
Direct Weighing as Ammonium Phosphomolybdate	30
Weighing as Magnesium Pyrophosphate	30
Solutions Required	30
ANALYSIS OF ASH	33
DETERMINATION OF SILICA	33
DETERMINATION OF IRON OXIDE, ALUMINA, AND TITANIC ACID	33
Solutions Required	35
DETERMINATION OF MANGANESE	36
Gravimetric Method	36
Volumetric Method—Sodium Bismuthate	37
Solutions Required	37
DETERMINATION OF LIME	38
DETERMINATION OF MAGNESIA	39
DETERMINATION OF SULPHUR TRIOXIDE	39
DETERMINATION OF PHOSPHORUS PENTOXIDE	40
DETERMINATION OF ALKALIES	40
Direct Method	41

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PAGE:

METHODS OF ANALYSIS—Continued 22
ANALYSIS OF ASH—Continued 33
Indirect Method 41
Error of Determining Alkalies by the Indirect Method.. 42
ULTIMATE ANALYSIS OF COAL 42
CARBON AND HYDROGEN 42
NITROGEN 43
ASH, SULPHUR, OXYGEN 44

METHODS FOR THE DETERMINATION OF THE CALORIFIC VALUE OF FUELS 45
DIRECT DETERMINATION BY MEANS OF THE OXYGEN OR SODIUM PEROXIDE BOMB CALORIMETER 46
Formula of Seyler 47
Formula of Diederich 47
Oxygen Bomb Calorimeter 47
Apparatus 47
Standardization 47
The Determination 49
The Corrections 51
Radiation 51
Acidity 52
Solutions Required 52
Sodium Peroxide Bomb Calorimeter 52
Apparatus 52
Determination 53
Radiation 54
Corrections 54
THERMAL VALUE CALCULATED FROM ULTIMATE ANALYSIS... 54
Dulong's Formula 54
THERMAL VALUE CALCULATED FROM PROXIMATE ANALYSIS.. 54

SAMPLING AND ANALYSIS OF BY-PRODUCTS 56
AMMONIA PRODUCTS 56
AMMONIA LIQUORS AND STILL WASTE 56
Sampling 56
Concentrated Ammonia Liquor 56

Digitized by Google

PAGE.
SAMPLING AND ANALYSIS OF BY-PRODUCTS—Continued.. 56
AMMONIA PRODUCTS—Continued..... 56
Weak Liquor..... 56
Still Waste..... 56
Specific Gravity..... 56
Free Ammonia..... 56
Total Ammonia..... 57
Fixed Ammonia..... 57
Sulphur..... 57
Total Sulphur..... 57
Sulphur Existing as Sulphate..... 57
Sulphur Existing as Sulphide..... 58
Pyridine..... 58
Free Lime..... 59
Distillation Method..... 59
Direct Titration..... 59
Chlorides in Weak Liquor..... 59
SATURATOR LIQUOR..... 60
Free Sulphuric Acid..... 60
Solutions Required..... 60
AMMONIUM SULPHATE..... 63
Sampling..... 63
Moisture..... 63
Free Acid..... 63
Total Ammonia..... 63
ANALYSIS OF COMMERCIAL SULPHURIC ACID..... 63
Sampling..... 63
Specific Gravity..... 64
Acid Content..... 64
Arsenic..... 64
Direct Reduction Method..... 64
Distillation Method..... 65
ANALYSIS OF LIME..... 65
Sampling..... 65
Active Lime..... 65
Distillation Method..... 67
Direct Titration Method..... 67
CRUDE TAR..... 67
SAMPLING..... 67

Digitized by Google

PAGE.

SAMPLING AND ANALYSIS OF BY-PRODUCTS—Continued.. 56
CRUDE TAR—Continued..... 67
SPECIFIC GRAVITY..... 68
WATER..... 68
FREE CARBON..... 70
Modified Underwriters' Extractor..... 70
Wiley Extractor..... 71
VOLATILE MATTER AND FIXED CARBON..... 71
ASH..... 71
VISCOSITY..... 71
COMPLETE DISTILLATION OF TAR..... 72
BENZOL PRODUCTS..... 72
GENERAL REMARKS..... 72
Boiling Point of Fractions..... 75
TESTING OF LIGHT OIL AND BENZOL..... 76
Sampling..... 76
Light Oil..... 76
Crude Benzols..... 77
Specific Gravity..... 77
Distillation..... 77
Total Sulphur..... 78
Refined Benzols..... 78
Pure Products..... 78
Acid Washing Test..... 79
DETERMINATION OF BENZOL IN GAS..... 80
DETERMINATION OF BENZOL IN BENZOLIZED AND DEBENZOLIZED OIL..... 81
PHYSICAL TESTS OF WASH OIL..... 83
Specific Gravity..... 83
Flash and Fire Point..... 83
Viscosity..... 83
Cloud Test..... 83
Fractional Distillation..... 83

Digitized by Google

PAGE.

LABORATORY METHOD FOR DETERMINING THE RELATIVE YIELDS OF COKE AND BY-PRODUCTS IN BITUMINOUS COAL BY THE PROGRESSIVE DRY DISTILLATION PROCESS 84

PREPARING THE COMBUSTION TUBE 84
SETTING UP ABSORPTION TRAIN 85
APPLICATION OF HEAT 85
DISCONNECTING THE TRAIN AND SUBSEQUENT MANIPULATION 86
CALCULATIONS 87
GAS CALCULATIONS 88
THERMAL VALUE OF THE GAS 88
SPECIFIC GRAVITY OF THE GAS 88
CALCULATIONS FOR REDUCTION OF OBSERVED VOLUME OF GAS TO STANDARD CONDITIONS 89
CALCULATION FOR DETERMINATION OF VOLUME OF HYDROGEN SULPHIDE 89
CALCULATION FOR DETERMINATION OF VOLUME OF CARBON DIOXIDE 89
REPORTING PER CENT PRACTICAL YIELDS 89
REPORTING EQUIVALENTS PER NET TON OF COAL 90

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PREFACE.

In conformity with the design of the officials of the United States Steel Corporation for the standardization of the methods employed in the sampling and analysis of all material encountered in their various lines of manufacture, the Chemists' Committee presents this compilation of standard Methods for the Sampling and Analysis of Coal, Coke and By-products.

In selecting the methods, particularly those referring to the proximate and other analyses of coal and coke, the Committee first compiled the data made available through its own members, after which it was submitted for approval to those laboratories of the Corporation most likely to be in a position to use or criticize.

In the By-product field, on account of its more recent introduction in this country, greater difficulty was encountered in compiling standard methods. Necessarily the problem had to be attacked in a different manner. The Committee has acted like a free lance in this respect, selecting those methods of by-product analyses that seemed to give the most consistent results and harmonize best with plant practice, regardless of where they were to be found.

No claim is made by the Committee for the permanency of the by-product methods. In the march of progress in the by-product world, obviously, it is impossible to formulate lasting methods, save in the fundamentals. Undoubtedly that part of the pamphlet will require revision and modification in a few years. This effort seems to embody the best everyday practice in use at the present time.

A special feature is the Progressive Dry Distillation Method, which should fill a long-felt want and which should commend itself to the various by-product plants and laboratories of the Corporation as an approved method for the evaluation of Coal and its By-products.

The services of the Sub-committee appointed for the purpose of preparing this pamphlet and composed of the following members: J. R. Campbell, Chairman, H. C. Frick Coke Co., Everson, Pa.; I. A. Nicholas, Secretary, Carnegie Steel Co., Clairton, Pa.; J. R. Harris, Tennessee Coal, Iron and Railroad Co., Ensley, Ala.; William Brady, South Works, Illinois Steel Co., South Chicago, Ill.; J. V. Freeman, Central Laboratory, Illinois Steel Co., Joliet, Ill.; C. N. Norris, Farrell Plant, Carnegie Steel Co., Farrell, Pa.; H. H. Jones, By-product Plant, Illinois Steel Co., Joliet, Ill., are gratefully acknowledged.

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SAMPLING.

On account of the variation in the composition of a seam of coal, the proper sampling of coal and the resultant coke is attended with more or less difficulty, and its importance cannot be emphasized too strongly. The impurities—sulphur, ash and phosphorus—occur mainly in the bone, slate and binder, several bands of which are often found in one seam, extending horizontally throughout the coal and varying in thickness from a fraction of an inch to a foot or more. In securing a representative sample, the main consideration should be to obtain a large sample, while that next in importance is to crush, quarter and pulverize it properly.

COAL SAMPLING.

SAMPLING AT MINES.

The coal sample should be taken and prepared, as far as possible, at the mine and the sampler provided with suitable tools therefor. Each mine or sampling point should be equipped with the following apparatus: An iron or steel plate, 10′ x 5′, shovel, steel maul, diameter of base 5″, trowel, quartering cross, length of dividing arm 36″, and a brush. With the use of such apparatus, a sample can be taken, mixed, crushed and quartered so that the sample sent to the laboratory for final treatment does not exceed ten (10) pounds in weight. In order to further minimize the laboratory preparation of the sample, a crusher may be installed at the sampling point, whereby the final sample is reduced both in weight and size of particles.

Development Sampling.

Most coals occur in horizontal layers and also in vertical laminations, and, when coal is being mined so that the face of the laminations is exposed, it is described as being on the "face;" when exposing the ends, it is described as being on the "butt." A face or butt sample is taken mainly for information relative to operating purposes. Channel samples should be taken preferably on the butt, for the reason that it is easier to cut a true channel there.

An average sample of the working face is obtained by means of the channel sample. Not fewer than three channel samples should be taken for every 100 wagons of output, in a fully developed mine. The channel is a cut 6″ wide and 2″ deep from top to bottom of the coal measure, on its face or butt. It may be found advantageous at times to remove the channel sample by sections (see illustration) in order to locate the impurities, and,

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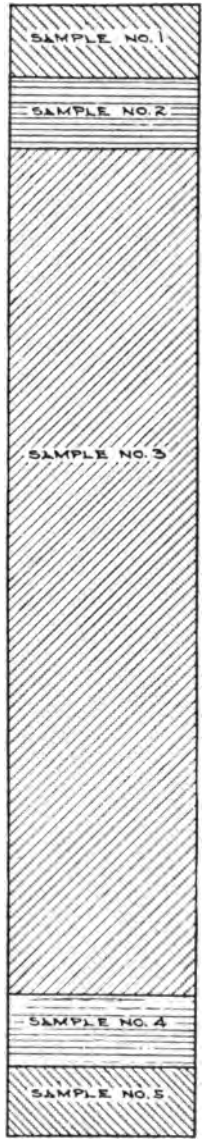

TYPICAL SECTION OF COAL SEAM

The horizontal divisions represent the different qualities of coal found in a seam, and they may vary both in physical appearance and chemical composition.

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after the individual sections have been analyzed, the average composition of the whole seam can be readily calculated.

The details of taking the channel sample are as follows: The face of the coal is cleaned thoroughly, if necessary, and the proposed sample is marked out on the face or butt of the coal. A strong canvas cloth is placed on the mine floor, and the sample is cut with a pick, starting preferably at the bottom.

After the sample is taken, the canvas is doubled over and the coal reduced by blows with the side of a pick or any other suitable tool. It should be reduced to pass a 2 mesh screen before the first quartering, and a 4 mesh screen before the second quartering, after which the sample may be quartered to approximately ten pounds without any further reduction in the size of the particles. The sample is then sent to the laboratory for final preparation as described under "Laboratory Preparation of Samples."

Sampling from the Pit Wagon or Tipple Chute.

An average sample of the mine-run coal is taken either from the pit wagons (mine cars) or from the chute as the coal runs from the tipple into the railroad car. The former method is generally used when the coal is to be converted into coke at the mines, while the latter is used when the coal is to be shipped in railroad cars. The pit wagons are sampled at any convenient point, either at the bottom or mouth of the pit or at the tipple. The sample is taken by removing a shovelful of coal from the top of each car, but at different positions on different cars successively. Thus, a shovelful is taken from the front of the first car, the middle of the second car, and rear of the third car, etc. The shovel used should not hold less than 2 pounds of coal. In a mine having an output of 600 wagons per day, 1200 pounds of coal should be obtained for the sample. If an accumulative sample is desired, to be prepared once each week, ten per cent. of the wagons hoisted each day should be sampled.

The sample is taken from the tipple chute by means of a shovel at stated intervals as the coal runs into the railroad car. The weight of the daily sample depends upon the output of the mine. The total daily sample should contain 2 pounds of coal for each pit wagon that is dumped at the tipple.

Run-of-mine coal contains variable proportions of lump and fine, and the object of taking a large sample in the manner just described is to obtain

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representative proportions of the lump and fine coal. Since the lumps in the sample vary in size, a representative mixture cannot be obtained unless the larger ones are crushed. Special attention should be given the relation of the size of the particles to the volume of the sample, and, since the correct relation has been carefully determined, the following methods describing these operations should be closely followed.

The lumps of the sample are crushed to one inch size, after which the whole is thoroughly mixed, coned and quartered successively until it is reduced to 100 pounds. The sample is then crushed and quartered alternately to the following weights and sizes respectively:

100 pounds—½"
50 pounds—¼"
25 pounds—⅛"

The final sample of 25 pounds is quartered until 10 pounds remain, which is sent to the laboratory for final preparation, as described under "Laboratory Preparation of Samples."

SAMPLING AT WORKS.

CAR SAMPLES. The sampler should be supplied with apparatus at the sampling point as described under "Sampling at the Mines." The preparation of the sample, mixing, crushing and quartering, is essentially the same as that already described. Ordinarily, the daily sample at By-Product Coke Oven Plants is taken as the crushed coal passes over the conveyor belt. This belt sample will serve for all ordinary purposes, however, in special cases, individual cars are sampled.

At other plants, the sample is taken either before the car is unloaded or while it is being unloaded. Whenever possible the sample should be taken while the car is being unloaded, as a more representative sample can be obtained in this way.

The weight of sample taken from one car varies according to the number of cars to be sampled. No coal sample, taken from cars, should be considered representative unless it weighs at least 1000 pounds. This applies to one car as well as to two or more cars which are to be combined as an average sample; e. g., if 40 cars are to be sampled and combined into one, the minimum

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weight taken from each car is 25 pounds, while if the analysis of an individual car is desired, the minimum weight of sample to be taken from the car is 1000 pounds.

After car samples are taken, in all cases, they are prepared as described under "Sampling from Pit Wagons and Tipple Chute."

SAMPLING AS CARS ARE BEING UNLOADED.

Hopper cars may be sampled after a part of their contents has been dropped, thereby exposing one or more faces from top to bottom of the coal. The sample is taken from the exposed face or faces by removing portions of coal of such volume and number as will give for the number of cars to be sampled, 1000 pounds.

Cars unloaded by hand are sampled from at least five exposed faces while the cars are being unloaded, by removing portions of coal of such volume and number as will give for the number of cars to be sampled, 1000 pounds. The five faces are distributed evenly throughout the length of the car, and extend the full width of the car from top to bottom of the coal.

SAMPLING BEFORE CARS ARE UNLOADED.

To obtain a representative sample of a car of coal before it is unloaded, is a difficult matter. A surface sample, in many cases, would not represent an average composition, due to the variation in the coal from the top to the bottom of the cars. Analytical results obtained on such a sample would be misleading. It is, therefore, recommended that, wherever possible, the surface sampling of individual cars be eliminated. If it is absolutely necessary to sample an individual car before it is unloaded, the method of sampling is as follows:

A trench is excavated, 2 feet in width and 2 feet in depth, along the median line of the car; another trench of similar dimensions is made at a right angle and at the center of the first. The sample is taken from the faces and bottom of the trenches, by removing portions of the coal, of such volume and number as will give 1000 pounds.

BELT SAMPLES.

Since coal for use in by-product coke ovens is crushed, it is a simple matter to obtain a representative sample after it is thus treated. The most convenient point for taking the sample is on the belt which conveys the coal from the crusher to the storage bins.

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The practice at certain by-product coke oven plants is to mix two or more kinds of coal; consequently, in order to obtain an intimate mixture, the coal is crushed until the greater portion will pass a ⅛" sieve.

In other plants, where but one kind of coal is used, it is unnecessary to crush the coal to this degree of fineness. However, in both cases, on account of the mixing that the coal undergoes during the crushing process, it is unnecessary to take as large a sample as those previously described.

The sample is taken by removing with a scoop or dipper, holding about ¾ pound of coal, a complete cross section of the crushed coal as it passes over the conveyor belt. If the speed of the belt and the depth of the coal do not permit sampling in this manner, a sample may be taken with a scoop or dipper at the two outer edges and at the center of the belt. In all cases, in removing the sample from the belt, the sampling tool should always penetrate through the layer of coal so that the fine particles lying directly on the belt are also included in the sample. Samples are taken at least every ten minutes, and more frequently in special cases, since not less than a 100-pound sample should be taken from every 1000 tons of coal passing over the belt. After the sample is collected, all over-size pieces are crushed to ¼" size, and it is then mixed and quartered to a 50-pound sample. This portion is crushed to ⅛" size, mixed and quartered until a 10-pound sample remains, which is sent to the laboratory and prepared as directed under "Laboratory Preparation of Sample."

COKE SAMPLING.

SAMPLING AT MINES—BEE-HIVE OVENS.

At least 10 per cent. of the ovens drawn each day should be sampled according to the accompanying sketch.

The sample of coke should be taken in such a manner that its analysis will yield results concordant with calculations based upon the analysis of the coal from which it was made; e. g., if the ash in the coal is 7 per cent. and the gross yield, coke and breeze, is 70 per cent., then the ash in the latter should be 10 per cent.

This method, described as follows, has proven satisfactory for bee-hive ovens:

The oven is divided into three imaginary concentric circles, in which the area of the inner circle corresponds very closely with that contained between the circumference of the inner and the next concentric circumference.

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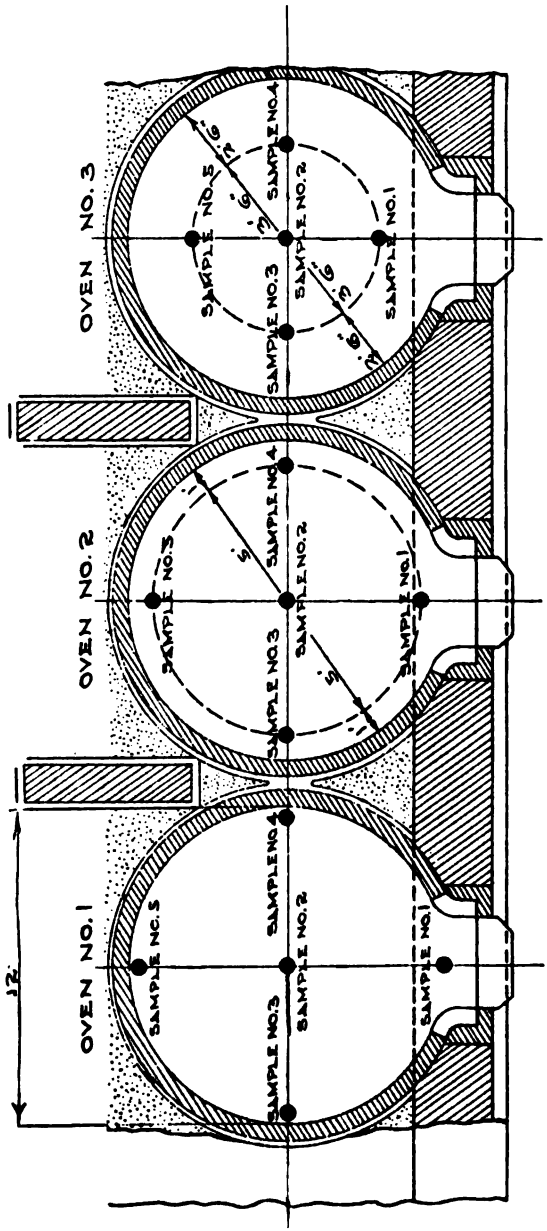

METHOD OF SAMPLING BEE HIVE OVEN COKE

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The circumference of the outlying concentric circle is the ring of the oven. It is a problem in mathematics, as shown by the following:

$$(1)\quad \text{Area of inner circle} = (7^2) \times \frac{3.1416}{4} = 38.5 \text{ sq. ft.}$$

$$(2)\quad \text{Area of next circle} = (10^2) \times \frac{3.1416}{4} = 78.5 \text{ sq. ft.}$$

$$(3)\quad \text{Area of bottom oven} = (12^2) \times \frac{3.1416}{4} = 113.0 \text{ sq. ft.}$$

113—78.5=34.5, area covered by first four samples on circle.

78.5—38.5=40.0, area covered by second four samples on circle.

38.5, area covered by third four samples on circle.

For all practical purposes, the zones as prescribed are sufficient in number to obtain a representative coke sample. It is manifestly fair to make the fifth sample the center of each oven sampled. It is entirely optional as to what point in the prescribed zones the samples are taken.

The practical application of this method of sampling is as follows:

The sampler designates the ovens to be sampled, usually by chalking the ovens with the numerals 1, 2, 3, etc., up to 15. A full length piece of coke, representing a vertical section, is taken from each oven to be sampled at the station designated thereon. For instance, the first full length piece of coke is taken in the front of oven No. 1, the second in the center of oven No. 2, the third at the left of oven No. 3, the fourth at the right of oven No. 4, and the fifth at the back of oven No. 5, all being taken near the ring wall; in the sixth, seventh, eighth, ninth and tenth ovens sampled, the same stations are observed, except that the samples are taken one foot from the ring wall; and in the eleventh, twelfth, thirteenth, fourteenth and fifteenth ovens sampled, the full length pieces are taken 2½ feet from the ring wall.

This operation is repeated until the requisite percentage of ovens is sampled. Where only a few ovens are sampled, it is often found advisable to take five full length pieces of coke from each. To get a true average from one oven, it is necessary to take the thirteen pieces from it. The individual samples of coke taken from the oven are usually too large and bulky, so that when the collection is made only a small "needle" is taken

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from each. This is best accomplished, with the use of a hammer and chisel, by removing a full length section about 1¼" square, and less than 2 pounds in weight.

The sample thus taken and collected is prepared after the manner described for coal samples, except in the use of the screen, since, in the case of coke, the 10 pound sample sent to the laboratory need pass only a ½" screen.

However, if crushers for the preparation of samples have been installed at the ovens, it is a good plan to reduce the sample to ¼" size.

Accumulative samples usually are taken, i. e., the daily samples are collected and prepared once each week from each Coke Works, and the results reported to the producers and consumers of the coke.

SAMPLING AT WORKS—BY-PRODUCT OVENS.

COKE PLANT SAMPLE. The coke plant sample is collected while cars are being loaded and is taken preferably as the coke runs from the screens into the railroad car. A sample of not less than 40 pounds is taken from each car loaded. This sample is taken preferably in a steel box large enough to contain a complete section of the area of the stream of coke. In case the stream is too wide to sample in this manner, samples may be taken at three different points, one in the center and one at each of the outer edges. In no case is a sample from less than approximately 75 per cent. of the cars loaded considered representative. The sample is then crushed and prepared as described under "Sampling at Mines—Bee-Hive Ovens."

BLAST FURNACE SAMPLE. Samples are taken from the cars as they are being unloaded by holding a pail in the stream. At least 25 per cent. of all cars unloaded should be sampled. After the sample is taken, it is prepared as described under "Coke Plant Samples."

This method of sampling is not satisfactory, and it is recommended that, wherever possible, the official samples be taken at the coke plant.

LABORATORY PREPARATION OF SAMPLE.

Considerable attention has been given recently to the contamination of coke samples with iron, due to the abrasion of the various types of apparatus used in the reduction of samples to the powdered form.

Investigation has proven that both a disc pulverizer and a bucking board (even of chrome steel) are worn to such an extent in the pulverization of samples, on account of the hardness of coke, that the use of apparatus of

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these types should be discontinued. By the use of a crusher fitted with manganese steel jaw plates, the sample can be safely crushed to ⅛" and further reduced to a 40 mesh powder by a machine constructed on the roll type. Abrasion can thus be minimized to a negligible quantity, and the use of such machines is recommended for laboratories which are required to prepare a large number of coke samples daily. In other laboratories, where the preparation of a few samples would not warrant the purchase of a roll machine for the pulverization of coke samples only, the use of a suitable mortar and pestle is recommended, as this method has proven both convenient and satisfactory.

METHOD—USE OF LABORATORY ROLL MACHINE.

The sample of coal or coke of approximately 10 pounds is passed through the laboratory crusher, adjusted to crush approximately to 10 mesh. It is then transferred to the sampling plate, thoroughly mixed and quartered, and opposite quarters rejected alternately until about 5 pounds remain. This sample is then passed through the roll machine, adjusted to crush to approximately 20 mesh, and is again mixed and quartered until about one pound remains. The final pulverization is conducted by adjusting the roll machine to crush to 40 mesh, when a sufficient amount of the sample is transferred to a bottle, and, after drying for one hour at a temperature of 105°C., is ready for analysis.

METHOD—USE OF DIAMOND STEEL MORTAR.

In laboratories not equipped with machinery, as described in the foregoing procedure, the sample of 10 pounds must be crushed necessarily by hand on a large plate (chrome steel is preferable).

This sample, crushed to ¼", is reduced by quartering to 2 pounds; this amount is crushed to ⅛", mixed and quartered to 1 pound, and then transferred to a 20 mesh sieve. The coarse portion remaining on the sieve is reduced in a diamond steel mortar (see print) so that it will also pass this sieve. The sample is again treated in this manner to pass a 30 and then a 40 mesh sieve.

It has been found by reducing coal and coke samples to the powdered form by this process, that abrasion was not so pronounced as when the use of the 20 and 30 mesh sieve was omitted.

DETERMINATION OF MOISTURE IN COAL AND COKE.

The sample of coal and coke for moisture determination is taken from the regular sample for analysis, by reserving one or more rejected quarters

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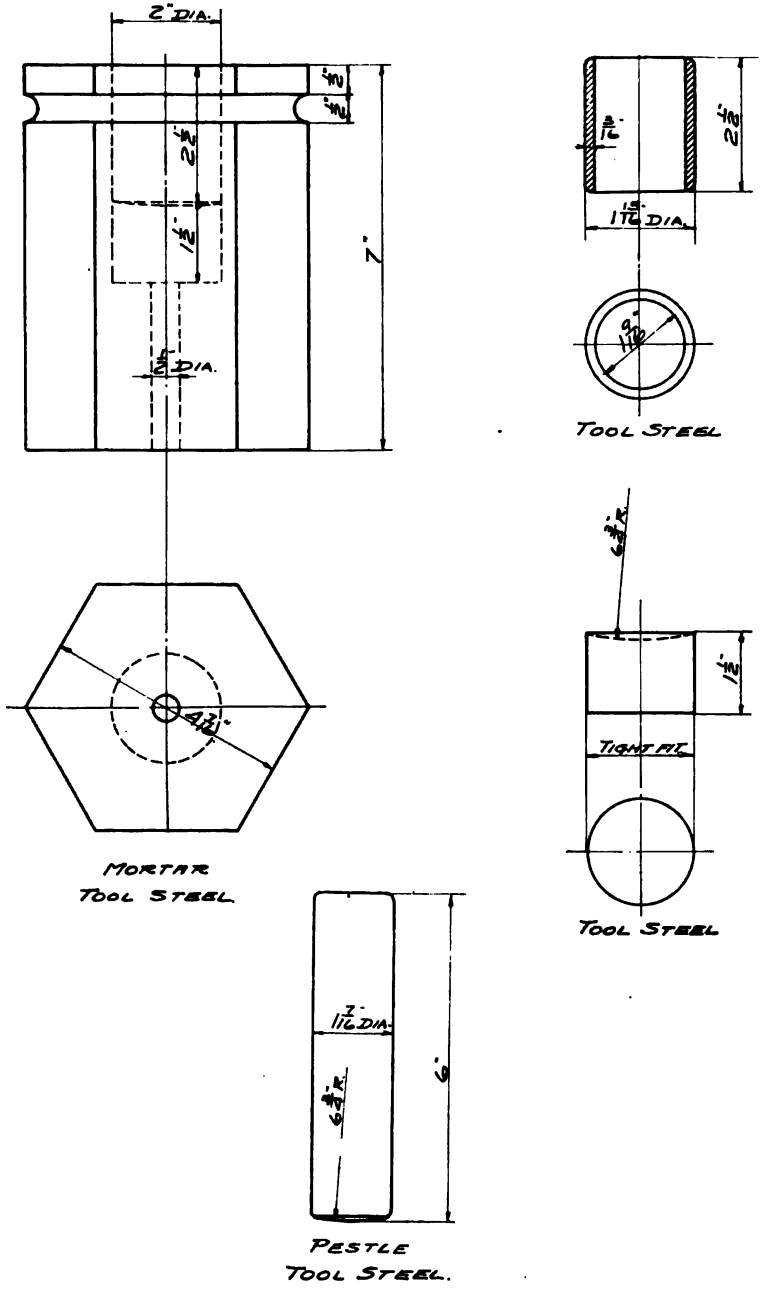

STEEL MORTAR AND PESTLE WITH BUSHING AND HARDENED STEEL PLATE, FOR PREPARING COAL AND COKE SAMPLES

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after the sample has been crushed to ½" size. Where it is the practice to collect accumulative samples, extending over a period of one week, the entire sample is crushed each day and a daily determination of moisture is made. The results are recorded and the average moisture content of accumulated sample is calculated from these determinations. In all cases, the sample for moisture should be prepared as soon as possible after the sample is taken.

Ten pounds or more of the regular sample are transferred to a tared pan. The pan and contents are then weighed and placed in a drying oven, heated preferably by steam, and maintained at a temperature of 105°C, until approximately constant weight is obtained. The loss in weight, divided by the weight of the wet sample, multiplied by 100, represents the per cent. of moisture in the sample.

DETERMINATION OF TRUE SPECIFIC GRAVITY OF COAL AND COKE.

Three to four grams of the coal or coke sample are transferred to a 50 cc. pycnometer containing approximately 30 cc. of distilled water. The mouth of the pycnometer is connected by means of rubber tubing to an aspirator and the contents of the bottle are gently boiled under partial vacuum until the air is completely expelled (2—3 hours).

The pycnometer is then almost filled with cold, boiled water, and, after cooling to room temperature, the stopper is inserted and the pycnometer and contents are weighed. The weight of the pycnometer, filled with water at the same temperature, is then determined. The true specific gravity is found by the following formula:

$$\text{True specific gravity} = \frac{W}{W-(W'-P)}$$

W=Weight of fuel.

W'=Weight of pycnometer+sample+water to fill.

P=Weight of pycnometer+water to fill.

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METHOD OF ANALYSIS.

GENERAL REMARKS.

In the following directions for analysis, it has been the desire to give the methods in considerable detail. In order to avoid constant repetition, however, the following statements are made herewith:

Whenever water is mentioned as a reagent, it is understood to mean distilled water. The strength of acids is indicated by the word "strong" or by the proportion, by volume, of strong acid to water in parenthesis. The word "strong" signifies that the ordinary concentrated acid and ammonia as received from the manufacturer are used. The specific gravities of sulphuric, nitric, hydrochloric acids and ammonia water would thus be 1.84, 1.42, 1.19 and .90, respectively. In giving the proportions in parenthesis the proportion of water is always given last. It is understood that not only the acids, but all the chemicals mentioned must be of C. P. grade.

PROXIMATE ANALYSIS.

VOLATILE MATTER—COAL.

The determination of volatile matter in coal by the ordinary laboratory methods has given results which, in many cases, have been misleading, since, in both the bee-hive and the by-product ovens, the actual yield of coke has been found greater than that indicated by calculations based on laboratory determinations. It is evident that it is impossible to devise a standard method that will harmonize actual coke yields with the theoretical yields as based upon laboratory analysis.

The progressive distillation method, hereinafter described, will give results quite comparable with those obtained in actual practice, provided that this laboratory determination is conducted, as far as possible, under the same conditions as those existing in actual coking practice. All other methods for the determination of volatile matter, two of which are described, yield results that are approximate only, but are useful for comparison of various kinds of coal. If close attention is given the details of manipulation in these methods, concordant results can be obtained.

Muffle Furnace Method.

The determination of volatile matter may be made in a muffle furnace, heated either by gas or electricity. In order to obtain concordant results, it is essential that all determinations be made in exactly the same manner, and that the details of the method be followed minutely. Proper temper-

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ature, and size of crucible, and a well-fitting lid, are important factors for the successful operation of this method.

Two grams of the dried sample are transferred to a weighed platinum crucible having a capacity of 30 cc., or, one gram of the sample is transferred to a platinum crucible having a capacity of 15-20 cc. The crucible is then covered with a tightly fitting lid. The crucible and contents, supported on a triangle, are placed in the front part of the muffle, where the temperature is about 500°C., and allowed to remain there, regardless of the time factor, until the charge ignites and the flame disappears. While the volatile matter is burning, the lid of the crucible should be kept in position by frequent tapping in order to prevent loss of carbon. If the charge does not ignite readily, it may be moved to a higher temperature, e. g., 560°C., for a few seconds, when it is withdrawn to its original position. When the volatile matter is consumed, the crucible is set into the hotter part of the muffle at a spot which has a temperature of 950°C., and is allowed to remain there for exactly three minutes. The crucible is then removed, cooled and weighed, and the loss in weight represents volatile matter.

The temperature of the muffle may be determined with the use of a pyrometer, but if such an instrument is not available, the higher temperature can be determined approximately with the use of potassium chromate, which melts at 940°C.

MEKER BURNER METHOD.

Where laboratories are not equipped with a muffle furnace, as described in the preceding method, a No. 4 Meker burner, properly adjusted, may be used. The air supply of the burner is first regulated so that a flame not less than 15 cm. in length is obtained. Since the determination by this method is conducted at a temperature of 950°C., the point in the flame having this temperature must first be ascertained. For this purpose, a platinum crucible, supported by a triangle, is placed in the flame, and a thermo-couple inserted through a small opening in the crucible cover, which for this purpose, may be nickel. The height of the crucible above the burner is adjusted until the temperature is 950°C., as indicated by the thermo-couple, the junction of which is kept in contact with the center of the bottom of the crucible. Potassium chromate may be used to indicate the temperature, as described in the preceding method.

The determination is conducted as follows: One gram of the sample is transferred to a platinum crucible having a capacity of 15-20 cc., and provided with a tightly fitting lid. The crucible and contents are placed in the flame

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and maintained there for seven minutes, at a temperature of 950°C. The crucible is then cooled, weighed, and the loss in weight represents volatile matter. In this method, as in the one previously described, the lid of the crucible is kept in position by frequent tapping.

VOLATILE MATTER—COKE.

Since properly carbonized coke contains practically no volatile matter, little importance is usually attached to this determination. However, practically all coke samples show varying amounts of loss on ignition. This is due partly to the expulsion of occluded gases, but mainly to oxidation of the sample during the ignition. To prevent oxidation, a smaller crucible should be used than those previously described, while the practice of "nesting" the crucibles, i. e., fitting a crucible into the one containing the sample, is also recommended, whereby the greater portion of air in the crucible is expelled. One gram of the sample is transferred to a 10 cc. platinum crucible provided with a tightly fitting cover or the crucible may be "nested." The volatile matter is then expelled by exposing the sample to a temperature of 950°C., either in a furnace or Meker burner flame, for three minutes. The loss in weight represents volatile matter.

ASH.

One gram of the sample, dried at 105°C., or five grams if the phosphorus is to be determined subsequently, are transferred to a crucible of alundum, porcelain or platinum. The sample is ignited in a furnace and in the case of a coal, the crucible and contents should be maintained at a low temperature until the volatile matter is nearly expelled, which is readily accomplished by placing the crucible in the front part of the furnace for ten to fifteen minutes, while coke samples may be placed in the hot part of the furnace without preliminary heating. The crucible and contents should be kept in the hot part of the furnace until the carbon has been completely consumed, which, in the case of a one gram sample, is usually accomplished in about one hour. The crucible is then cooled, and its contents transferred to a tared watch glass, by means of a brush. The percentage of ash is found by dividing the weight of ash by the amount of sample used and multiplying the quotient by 100.

FIXED CARBON.

The difference obtained by subtracting the sum of the percentage of ash and volatile matter from 100 represents the fixed carbon.

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DETERMINATION OF METALLIC IRON DUE TO ABRASION IN COAL AND COKE

In using any apparatus for pulverizing the samples, the amount of contamination from abrasion of the pulverizing surfaces should always be investigated.

When the apparent ash and the per cent. of metallic iron in the sample are known, the true ash is readily obtained. The determination of the metallic iron is based upon the fact that it is dissolved by a copper salt, while the combined iron is undissolved.

Five grams of the sample, dried at 105°C., are placed in a No. 2 beaker, and 75 cc. of a 5% solution of copper sulphate added. The contents of the beaker are boiled for ten minutes, filtered, and the residue is washed six times with hot water. The filtrate is acidified with a few drops of hydrochloric acid and then treated with 2 cc. of strong nitric acid. The solution is boiled for a few minutes, whereby the iron is oxidized. A slight excess of ammonia is then added, and the boiling continued for one minute. The iron, precipitated as the hydrate, is removed by filtration and washed six times with hot water. The ferric hydrate is dissolved with hydrochloric acid (1-1), reprecipitated to free it from copper salts, and determined either gravimetrically or volumetrically, as described under "Analysis of Ash."

The iron found is calculated to ferric oxide, as it burns to the oxide in the ash determination. This weight of ferric oxide is deducted from the ash and the difference divided by the quantity of coke used, minus the metallic iron as found, represents the true ash.

As there is always some iron present in copper sulphate, a blank determination should be made on some multiple of 75 cc.—the amount used in the method.

There is generally found a small quantity of metallic iron in coke as it comes from the oven. Usually the amount present is so small that it is negligible; this, however, may be determined in a sample that has been prepared in an agate mortar and a correction, if necessary, is applied to the true ash.

Example:

.1046 wt. of apparent ash in sample.
5 grams.

.5230 wt. of apparent ash in 5 grams.

.0185 wt. of ferric oxide (on 5 grams).

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.0007 blank on 75 cc.

.0178 corrected ferric oxide.

.7 ferric oxide to iron.

.0125 iron (on 5 grams).

5.0000 grams of coke.
.0125 iron (on 5 grams),

4.9875 actual coke.

.5230 wt. of apparent ash (on 5 grams).
.0178 wt. of corrected ferric oxide.

.5052 corrected wt. of ash.

.5052 divided by 4.9875 x 100=10.13% ash.

DETERMINATION OF SULPHUR.

ESCHKA METHOD. One gram of the sample or the factor weight, 1.374 grams, is transferred to a shallow porcelain or platinum dish of approximately 35 cc. capacity, and 6½ cm. in diameter, containing about 1.5 grams of Eschka mixture (two parts magnesium oxide, one part sodium carbonate). The contents of the dish are thoroughly mixed by stirring with a glass rod, and after brushing off adhering particles from the rod, approximately 1.5 grams of Eschka mixture are sprinkled over the surface of the contents of the dish. The sample is placed in the front of a gas heated muffle furnace, or in an electric furnace heated to a dull red, and maintained there for twenty minutes, when it is exposed to approximately 800°C. until the carbon is consumed.

The dish is then removed from the furnace, cooled, its contents crushed, if necessary, and transferred directly to an 11 cm. qualitative filter paper contained in a Bunsen filtering funnel. The small particles adhering to the sides of the dish are moistened with hot water, when they are readily detached by a glass rod and are transferred to the filter paper. The dish is washed with hot water, scrubbed with a "policeman," the washings transferred to the paper, and the paper and contents washed six times with hot water. The filtrate received in a No. 2 beaker or a 300 cc. wide-mouth Erlenmeyer flask, should now have a volume of approximately 150 cc.

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To the beaker, or flask, are added 10 cc. of water, saturated with bromine, followed by 5 cc. of concentrated hydrochloric acid. Heat is then applied, and, when the solution has reached the boiling point, 10 cc. of a 10% solution of barium chloride are added and the solution is gently boiled for thirty minutes. The beaker and contents are removed from the heat and allowed to stand at a temperature of approximately 70°C. for one to two hours, when the precipitate of barium sulphate is ready for filtration. The supernatant liquid is decanted through a double ashless 9 cm. filter paper, and the residue of barium sulphate in the beaker is transferred to the filter paper by means of a jet of dilute hydrochloric acid (1%). The paper and contents are washed with hot water until the washings, when tested with silver nitrate solution, are shown to be free from chlorides. The paper containing the precipitate is then transferred to a platinum crucible and ignited, uncovered, at a low temperature, until the paper is consumed, and finally at a higher temperature for ten minutes.

The contents of the crucible are brushed upon a tared watch glass and weighed. The weight of barium sulphate, multiplied by 13.74, yields the per cent. of sulphur present if one gram of the sample was used. If the factor weight of the sample was used, the weight of barium sulphate is multiplied by 10.

It has been the custom in some laboratories to report the percentage of sulphur in coal and coke to the third decimal place. It is recommended that this practice be discontinued and that the percentage of sulphur in coal and coke be reported only to the second decimal place.

The filtrate should always be examined for barium sulphate, as traces will, at times, pass through the filter paper. For very accurate work, therefore, the filtrate is set aside for twelve hours, and any precipitate that may have settled out is removed by filtration and the weight added to that already obtained.

In order to determine traces of sulphur in the reagents used, a blank test should always be made in the same manner as the actual determination, and the necessary correction applied.

DETERMINATION OF PHOSPHORUS.

PREPARATORY TREATMENT OF THE SAMPLE FOR THE PRECIPITATION OF PHOSPHORUS.

HYDROFLUORIC ACID METHOD.

The ash from 2 to 5 grams of coke is treated in a platinum dish, or crucible, of 30 to 50 cc. capacity, with 5 cc. of hydrochloric acid (sp. gr. 1.10)

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and 10 to 15 cc. of hydrofluoric acid (48% HF). Heat is applied until the residue is dissolved, when the solution is evaporated to dryness in a good hood. The residue is heated to the expulsion of the hydrofluoric acid, but not baked, as this would render the residue difficultly soluble in the subsequent treatment. Ten to 15 cc. of hydrochloric acid (sp. gr. 1.10) are added to the crucible, or dish, and heat is applied until the contents are dissolved. The solution is transferred to a dish, or beaker, 5 cc. of nitric acid (sp. gr. 1.42) are added and the solution is boiled until completely oxidized A small amount of paper pulp is added to entangle any finely divided particles which might run through the filter paper in the subsequent filtration. The solution is filtered, while hot, through an 11 cm. qualitative filter paper, and the filtrate retained in an 8-ounce Erlenmeyer or Florence flask. The paper and residue are washed three times with hot water. If a residue remains on the filter paper, it should be examined for traces of phosphorus, by fusing, after ignition, with a small amount of sodium carbonate. The fusion is dissolved in water, filtered, and the filtrates are combined. The solution is now ready for the precipitation of phosphorus.

Fifteen cc. of sulphuric acid (1-15), or 2 cc. of nitric acid (sp. gr. 1.20) may be used, in order to dissolve the ash, instead of 5 cc. of hydrochloric acid as specified. If sulphuric or nitric is used, the residue, after expelling the hydrofluoric acid, may be treated directly with 25 cc. of nitric acid (1.20 sp. gr.), and the determination then completed as just described.

FUSION METHOD.

The ash from 2 to 5 grams of coke, in a platinum crucible of 30 cc. capacity, is fused with 10 to 25 grams of sodium carbonate and a few crystals of sodium or potassium nitrate, or the ash from 2 to 5 grams of coke in a 5-inch porcelain dish is digested by means of heat, with 10 to 25 cc. of hydrochloric acid (sp. gr. 1.19) for 20 minutes. When cool, the solution is filtered, the residue washed and the filtrate set aside. The residue is ignited and fused as described above. The fusion in either case is transferred to a covered porcelain dish containing about 25 cc. of hot water. When the fusion has disintegrated, the contents of the dish, if from the direct fusion of the ash, are acidified with hydrochloric acid (sp. gr. 1.19); if the fusion is from the digested ash, the contents of the dish are acidified with the filtrate that was set aside, care being taken to transfer all of the filtrate to the disintegrated fusion. The small residue adhering to the crucible is dissolved in hot water and hydrochloric acid (sp. gr. 1.19) and the solution and washings added to the main solutions in the dish. The acidified solution from either fusion is evaporated to dryness and baked at a temperature not exceeding 120°C. for

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30 minutes. The baked residue is moistened with hydrochloric acid (sp. gr. 1.10), heat applied until iron salts are in solution, water is added, and the solution boiled until sodium salts are dissolved. The solution is filtered, washed, and to the filtrate ammonium hydroxide is added in slight excess. After boiling for a few minutes, the precipitate is allowed to settle.

The precipitate is collected on a 9 cm. qualitative filter paper and washed with hot water. The washed precipitate is dissolved on the filter paper in hot nitric acid (sp. gr. 1.20), the paper thoroughly washed and the solution and washings are retained in an 8-ounce Erlenmeyer or Florence flask; or, the baked residue from the fusion is moistened with hydrochloric acid (sp. gr. 1.19), heat applied until the iron salts are dissolved when 30 cc. nitric acid (sp. gr. 1.42) are added, and the contents of the dish boiled until the disappearance of the brown fumes. The solution is diluted, filtered, washed, the filtrate and washings passing into an 8-ounce Erlenmeyer or Florence flask. The solution is now ready for the precipitation of the phosphorus.

PRECIPITATION OF PHOSPHORUS.

To the solution in the Erlenmeyer or Florence flask, a slight excess of ammonium hydroxide (sp. gr. .90) over the amount necessary to precipitate the iron and aluminum is added. The flask is shaken, the precipitate is just dissolved by adding nitric acid (sp. gr. 1.42), and an excess of 2 to 5 cc. is added. The solution is heated or cooled to 80° C., and 10 to 40 cc. of ammonium molybdate solution are added. The flask is shaken for 5 minutes, by hand or machine, and is then set aside to allow the precipitate to settle. The determination may then be completed by any of the following methods:

FINAL DETERMINATION OF PHOSPHORUS.

Volumetric Methods.

ACID ALKALI TITRATION.

The precipitate of ammonium phosphomolybdate, after settling, is collected upon a 9 cm. qualitative filter paper, washed with 2% nitric acid until free from iron solution and finally with a 1% potassium nitrate solution until free from acid.

The titration is made in a No. 2 beaker or in the flask in which the precipitation was made. In the former case, the operator should exercise care in completely removing any precipitate adhering to the flask by means of a long "policeman," while in the latter case, the flask should be thoroughly

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washed with potassium nitrate solution until the acid is completely removed.

The filter paper and precipitate are transferred to the titrating vessel and treated with an excess (1 to 2 cc.) of standard sodium hydroxide solution. The filter paper is macerated with a glass rod if the titration is performed in a beaker, or, if made in a flask, a clean rubber stopper is inserted and the contents shaken vigorously until the paper is disintegrated and the solution of the precipitate is complete. The solution is diluted to approximately 100 cc., three drops of phenolphthalein solution are added, followed by the standard nitric acid until the pink color disappears. If preferred, the standard alkali may be finally added to a faint permanent pink end point.

POTASSIUM PERMANGANATE TITRATION.

The yellow precipitate is collected on a filter and washed with ammonium sulphate solution or a two per cent. sulphuric acid solution, until free from iron and molybdenum salts. The funnel containing the precipitate is transferred to the flask in which the precipitation was made, and the precipitate is dissolved in dilute ammonia (1-3). The resulting solution should not exceed 25 cc. Eight grams of granulated zinc (20 mesh) are added, followed by 75 cc. of sulphuric acid (1-4). The solution is boiled gently until reduction is complete. It is then filtered through glass wool or asbestos, and the filtrate is received in a beaker. The flask and filter are washed thoroughly with cold water. The solution is titrated with standard potassium permanganate solution until a slight permanent pink tint is obtained. The percentage of phosphorus is calculated from the number of cc. required.

By Gravimetric Methods.

DIRECT WEIGHING AS AMMONIUM PHOSPHOMOLYBDATE.

The yellow precipitate is transferred to 9 cm. ashless filter paper, which has been previously dried for at least half an hour at 110° to 120° C., and weighed between watch glasses. The precipitate is then washed thoroughly with a 2% solution of nitric acid, dried for one hour at the above temperature and weighed between glasses; 1.63% of the weight of the precipitate equals the per cent. of phosphorus.

WEIGHING AS MAGNESIUM PYROPHOSPHATE.

The yellow precipitate is collected upon a 9 cm. ashless filter paper and washed with a 2% solution of nitric acid until free from iron and molybdenum

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salts. It is then dissolved on the filter paper with the smallest possible amount of hot ammonium citrate solution, and the filtrate is received in a No. 0 beaker. The filter paper is washed several times with hot water, after which 5 to 10 cc. of magnesia mixture are poured through, and the filtrate in the small beaker is thoroughly mixed and allowed to stand for at least three hours, or, if possible, over night. The precipitate is collected on an ashless filter paper, washed with dilute ammonia (one part ammonium hydroxide, sp. gr. .90, to 3 parts distilled water), and ignited at a low temperature until the carbon of the filter paper is destroyed. It is then ignited at the highest temperature of the Meker burner or muffle furnace, cooled and weighed as magnesium pyrophosphate, 27.87% of which is phosphorus.

When extreme accuracy is desired, the precipitate is dissolved on the filter with the least possible amount of cold hydrochloric acid (1-1). The solution thus obtained is diluted to about 100 cc., several drops of magnesia mixture are added, followed by ammonia, drop by drop, with constant stirring. When the crystalline precipitate is formed, 5 cc. excess of strong ammonia are added. The solution and precipitate are agitated and allowed to stand for several hours. The precipitate is then collected on a filter, washed thoroughly with dilute ammonia (1-4), and the determination is completed as above described.

SOLUTIONS REQUIRED.

Ammonium Molybdate.

(a) Molybdic Acid—85%..... 65 grams.
Ammonium Hydroxide (.90 sp. gr.)...143 cc.
Water.....142 cc.
Nitric Acid (1.20 sp. gr.).....715 cc.

(b) Molybdic Acid—100%..... 56 grams.
Ammonium Hydroxide (.90 sp. gr.)...143 cc.
Water.....142 cc.
Nitric Acid (1.20 sp. gr.).....715 cc.

The molybdic acid is dissolved in the mixture of ammonia and water. This solution is slowly added, with constant stirring, to the nitric acid. If the solution is cloudy, two drops of a 20% solution of ammonium phosphate are added, the precipitate which forms is allowed to settle, and the solution is filtered into bottles, and, if necessary, refiltered just before using.

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Sodium Hydroxide Standard.

Sodium Hydroxide, c. p.	65.9 grams.
Water	1000 cc.

100 cc. of this solution are diluted to 1000 cc. to give approximately correct strength.

Nitric Acid Standard.

Nitric Acid (1.42 sp. gr.)	10 cc.
Water	1000 cc.

The standard acid and alkali solutions are adjusted so that they exactly agree, and one cc. is equivalent to one-hundredth per cent. phosphorus when two grams of the sample are used. Simple calculations permit the use of these solutions for varying weights of sample. For confirming the solutions, the use of the Corporation Standard iron ore of known phosphorus content is recommended. The standard acid and alkali solutions should be frequently checked against each other.

Phenolphthalein Indicator.

Phenolphthalein	1 gram.
Alcohol	1000 cc.

Ammonium Citrate.

Ammonium Hydroxide (.90 sp. gr.)	350 cc.
Water	650 cc.
Citric Acid, c. p.	50 grams.

Magnesia Mixture.

Magnesium Sulphate, c. p.	84 grams.
Ammonium Chloride, c. p.	250 grams.
Water	665 cc.
Ammonium Hydroxide (.90 sp. gr)	335 cc.

Ammonium Sulphate.

Water	960 cc.
Ammonium Hydroxide (.90 sp. gr.)	15 cc.
Sulphuric Acid (1.84 sp. gr.)	25 cc.

Potassium Permanganate Standard.

Potassium Permanganate, c. p.	4.26 grams.
Water	1000 cc.

This solution is standardized by means of the Corporation Standard Iron Ore of known phosphorus content.

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ANALYSIS OF ASH.

DETERMINATION OF SILICA.

The ash obtained from the ignition of five grams of coal or coke is transferred to a platinum crucible, and mixed with sodium carbonate, approximately six times the weight of ash. Heat is applied until the ash is completely decomposed, when the fusion is transferred to a 12 cm. dish. Hot water is added and a gentle heat applied until the fusion is disintegrated, when 50 cc. of concentrated hydrochloric acid are added. The contents of the dish are evaporated to dryness, and the residue is baked at a temperature not exceeding 120° C. for fifteen minutes. The dish is cooled, the residue moistened with a few drops of hydrochloric acid, and heated gently until the iron is dissolved, after which approximately 75 cc. of hot water are added. Heat is applied, and, when the soluble salts are dissolved, the silica is removed by filtration. The filter and contents are washed alternately with hot water and dilute hydrochloric acid (1-2) until the iron stain is removed and finally with hot water until the washings are free from chlorides. In order to recover traces of silica which remain in solution, the filtrate should be evaporated to dryness, baked, the silica separated by filtration and washed as just described. The filtrate and washings, contained in a No. 3 beaker, are reserved for other determinations.

The silica residues are combined, ignited in a platinum crucible and weighed. The residue in the crucible is treated with 2 drops of sulphuric acid (1-1) and 5 cc. of hydrofluoric acid. The solution is evaporated carefully to dryness and then heated to the expulsion of sulphuric anhydride. The crucible is again weighed and the difference between the weight of crucible and contents before and after volatilization, is calculated to per cent. silica.

DETERMINATION OF IRON OXIDE, ALUMINA, AND TITANIC ACID.

The residue in the platinum crucible, after the volatilization of the silica, usually consists of a small amount of iron oxide and titanic acid. This can either be added to the weight of the oxides, which are determined as hereinafter described, or it can be determined with the main oxides. For the latter purpose, to the residue in the crucible, approximately one gram of sodium carbonate is added and a fusion is made as previously described. The fusion is added to the filtrate from the silica which has been reserved for the determination of other elements. Strong ammonia is added to the solution until a precipitate is obtained that does not disappear after vigorous stirring, after which an excess of 1 cc. of strong ammonia is

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added. Heat is then applied and the contents of the beaker are boiled for one minute. The precipitated hydrates of iron, aluminum and titanium are allowed to settle, when they are removed by filtration and washed 4 times with hot water. The filtrate is reserved in a No. 4 beaker, while the precipitate on the filter is dissolved with hot hydrochloric acid (1-1), and the solution is retained in the same beaker in which the first precipitation was made. The solution of the hydrates is treated with strong ammonia, and the reprecipitated hydrates are filtered and washed, as just described. The filtrate is combined with that obtained from the first precipitation, and the whole retained for the determination of other elements. The precipitate of the hydrates is washed an additional four times with hot water, and these washings are discarded. The paper and contents are transferred to a platinum crucible, ignited and weighed. This weight represents iron oxide, alumina titanic acid, and phosphoric acid. The phosphoric acid being very small may be disregarded. The per cent. of iron oxide and titanic acid is found by a direct determination, while the alumina is obtained by difference, according to the following equation:

Total oxides—(iron oxide+titanic acid)=Alumina.

In order to determine the iron oxide, the residue in the platinum crucible is transferred to a No. 2 beaker and treated with 15 cc. of strong hydrochloric acid and three drops of stannous chloride solution. The beaker and contents are then gently heated for approximately one hour or until the iron oxide is completely dissolved, when the solution is concentrated to a volume of approximately 7 cc. The iron is then determined by titration with potassium bichromate or permanganate in the following manner:

Stannous chloride is added to the solution, drop by drop, until the color, due to the ferric chloride, finally disappears. One drop is then added in excess. The solution is transferred to a No. 3 beaker and diluted to approximately 200 cc. with cold water, 5 cc. of mercuric chloride are added and the solution is thoroughly stirred. Standard bichromate solution, almost sufficient to oxidize the iron, is added, and a drop is transferred to a drop of the external indicator—potassium ferricyanide solution—contained on a test plate; the addition of the titrating solution is then continued with frequent tests, until the blue color of the ferrous iron has given way to the yellow or brown of the oxidized iron; or standard permanganate solution is added with constant stirring until the pink tint reluctantly disappears. The solution is then added drop by drop to the final pink end point which may be the first stable pink coloration, or a definite excess of one or more drops as desired. The number of cc. of standard bichromate

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or permanganate solution required for the titration, multiplied by the value of 1 cc. in terms of iron, represents the percentage of iron in the ash. The percentage of iron, divided by .7, represents the percentage of iron oxide.

For the determination of titanic acid another sample is used. The ash in a platinum crucible obtained from the ignition of five grams of the sample is treated with two drops of strong sulphuric acid and five cc. of hydrofluoric acid. The solution is evaporated to dryness and then heated to the expulsion of sulphuric anhydride. The residue is fused with sodium carbonate, the fusion transferred to a No. 2 beaker and dissolved with strong hydrochloric acid. The titanic acid is then determined colorimetrically as follows:

The solution is transferred to a suitable comparison tube, 5 cc. of hydrogen peroxide and 2 cc. of a 50% solution of phosphoric acid are added, when the whole is diluted to a definite volume and mixed. Into a similar tube are placed 5 cc. of hydrogen peroxide, and hydrochloric acid (5%) is added until the volume of the mixture is slightly smaller than that contained in the other tube. The standard titanium sulphate solution is now added from a burette, till, after thorough mixing, the color matches that of the other solution, when it is diluted to the same volume, again thoroughly mixed, and its color compared with the other solution. The determination is completed by carefully matching the colors after the addition, if necessary, of one or more drops of the standard solution. The number of cc. of the standard solution used indicates the titanic acid present.

SOLUTIONS REQUIRED.

Stannous Chloride.

Stannous Chloride	250 grams.
Hydrochloric Acid (1.19 sp. gr.)	500 cc.
Water	500 cc.

Mercuric Chlorid.—Cold Saturated Solution.

Potassium Ferricyanide Indicator.

Potassium Ferricyanide	1 gram.
Water	1000 cc.

Potassium Bichromate Standard.

Potassium Bichromate	4.45 grams.
Water	1000 cc.

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Potassium Permanganate Standard.

Potassium Permanganate..... 2.85 grams.
Water..... ..1000 cc.

The bichromate and permanganate solutions are standardized against the Corporation Iron Ore Standard under the same conditions as are maintained in an actual analysis.

Standard Titanium Sulphate Solution.

Twenty-six-hundredths of a gram of ignited titanic acid (Mercks) are fused with six grams of sodium carbonate, the fusion is disintegrated in 50 cc. of water in a No. 2 beaker and the crucible and lid are placed therein. After warming for an hour with 100 cc. of dilute sulphuric acid (1-4), solution will usually be complete. This solution is transferred to a 250 cc. volumetric flask and diluted to the mark with water. The purity of the titanic acid may be found, and the solution thus standardized, by transferring 50 cc. of this solution to a No. 5 beaker. Ammonia is then added until a flocculent precipitate is formed and the solution is yet acid to litmus. One and a half cc. of strong hydrochloric acid are added, followed by 30 cc. of sodium thiosulphate solution (20%) and 250 cc. of water. The solution is boiled for ten minutes and the precipitated titanic acid is allowed to settle, after which it is transferred to a filter, washed ten times with hot 2% acetic acid, ignited and weighed as titanic acid. This weight of titanic acid, divided by 50 represents the amount of titanic acid present in 1 cc. of the standard solution.

DETERMINATION OF MANGANESE.

The manganese may be determined gravimetrically in the filtrate reserved after the separation of the oxides, or, volumetrically, by the bismuthate method, on a separate sample.

GRAVIMETRIC METHOD.

The filtrate from the hydrates is evaporated to a volume of approximately 100 cc., when a solution of one gram of ammonium persulphate is added, followed by 15 cc. of strong ammonia. The solution is then stirred vigorously. After boiling for about ten minutes, the precipitate is collected on a filter paper and washed with hot water. The filtrate is retained in a No. 3 beaker for the determination of lime and magnesia. The paper and contents are ignited in a weighed platinum crucible, at first at a gentle heat and then at the highest temperature of a muffle furnace or blast lamp for not less than 30 minutes, and weighed as mangano-manganic oxide. The weight of

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this oxide, multiplied by the factor .9301, furnishes the weight of manganous oxide.

The oxide in the crucible should be examined for traces of silica by dissolving in hydrochloric acid (1-1). The silica is removed by filtration, washed, ignited and weighed, and the necessary correction applied to the weight of the mangano-manganic oxide.

VOLUMETRIC METHOD—BISMUTHATE METHOD.

The ash obtained from the ignition of one gram of the sample is treated in a platinum crucible with a few drops of sulphuric acid (1-1) and 5 cc. of hydrofluoric acid. The contents of the crucible are evaporated until fumes of sulphuric anhydride are expelled. About two grams of potassium bisulphate are then added and the residue heated at the fusion point for ten minutes. The crucible and contents are then allowed to cool and the fusion is transferred to a No. 2 beaker containing 50 cc. of water and 20 cc. of concentrated nitric acid. A gentle heat is applied until solution of the fusion is effected when small quantities of sodium bismuthate are successively added until the pink color of permanganic acid persists or the brown oxide of manganese is precipitated upon boiling. Ammonium bisulphite solution (5%) is now added, a few drops at a time, until the solution becomes clear and the excess of the reducing agent is expelled by continued boiling. The contents of the beaker are cooled to room temperature. Five-tenths to one gram of sodium bismuthate is added and the solution decanted through an asbestos filter, and the beaker and filter washed with 3% nitric acid until the washings are colorless. The filtrate and washings are now transferred to a No. 2 beaker. A measured excess of approximately 10 cc. of a thirtieth normal ferrous sulphate solution is added and the excess thereof determined by a thirtieth normal potassium permanganate solution. The difference between the volume of permanganate solution required and that equivalent to the total volume of ferrous sulphate solution added, is multiplied by the value in manganese of 1 cc. of the standard permanganate solution. The result thus obtained is calculated to the percentage of manganese in the sample.

SOLUTIONS REQUIRED.

Sodium Oxalate Solution.

Sodium Oxalate ..... 1 gram.
Water.....1000 cc.

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Thirtieth Normal Potassium Permanganate Solution.

Potassium Permanganate..... ..... 1.06 grams.
Water.....1000 cc.

The solution is allowed to stand for 24 hours before standardizing. For this purpose, 100 cc. of the sodium oxalate solution are transferred to a No. 3 beaker containing 20 cc. of sulphuric acid (one part acid to one part water by volume). The contents of the beaker are heated to 80° C., and the standard permanganate solution added slowly at first and then rapidly until a permanent pink tint is obtained. The percentage of manganese in 1 cc. of the standard permanganate solution is found by the following calculation:

$$\frac{1.6397}{\text{(Volume of permanganate solution required to oxidize 100 cc. of the sodium oxalate solution.)}}$$

Thirtieth Normal Ferrous Ammonium Sulphate Solution.

Ferrous Ammonium Sulphate..... 13.07 grams.
Water..... 920 cc.
Sulphuric Acid—Strong..... 80 cc.

DETERMINATION OF LIME.

The filtrate from the manganese is heated to the boiling point, 10 cc. of strong ammonia and 5 cc. of a saturated solution of ammonium oxalate are added, and the heating is continued until the volume of the solution is reduced to about 100 cc. Five cc. of strong ammonia are now added and the solution is boiled for about ten minutes. The precipitate is collected on a filter and washed until free from chlorides. When the lime and magnesia are low, as in normal coal or coke samples, only the first four washings are allowed to flow into the filtrate, the object being to keep the filtrate as concentrated as possible for the magnesia determination.

The filter and contents are placed in a weighed platinum crucible, ignited, cooled in a desiccator, and weighed as calcium oxide.

The calcium oxide so obtained is liable to be contaminated with a small amount of silica and, when extreme accuracy is desired, the ignited and weighed precipitate is dissolved in warm, dilute hydrochloric acid (1-1), and the solution evaporated to dryness. The residue is dissolved in dilute hydrochloric acid (1-2), the silica is determined and deducted from the previous weight.

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DETERMINATION OF MAGNESIA.

The filtrate from the calcium oxalate, which should not exceed 200 cc. in volume, is made slightly acid with strong hydrochloric acid and 5 cc. of a 10% solution of ammonium phosphate are added. To the cold solution, strong ammonia is added, drop by drop, with constant stirring until distinctly alkaline. The solution is stirred at intervals for two or three hours, or preferably agitated mechanically for about one hour. If permissible, it is then allowed to stand in a cool place over night. The time required for complete precipitation is shorter, the greater the quantity of magnesium present. The precipitate is removed by filtration, washed with dilute ammonia (1-4), ignited, and weighed. When extreme accuracy is desired, however, the precipitate is dissolved on the filter with the least possible amount of cold, dilute hydrochloric acid (1-1). The solution thus obtained is diluted to about 100 cc., several drops of ammonium phosphate solution are added, followed by ammonia, drop by drop, with constant stirring. When the crystalline precipitate is formed, 5 cc. excess of strong ammonia are added. The solution and precipitate are agitated and allowed to stand for several hours. The precipitate is collected on a filter and washed thoroughly with dilute ammonia (1-4) until the washings, when acidified with nitric acid, are free from chlorides. The paper and contents are placed in a weighed platinum crucible and ignited at a low temperature until the filter is destroyed, and finally at the highest temperature of the Meker burner, muffle furnace or blast lamp and weighed as magnesium pyrophosphate, containing 36.21% magnesia.

DETERMINATION OF SULPHUR TRIOXIDE.

The ash will contain a portion of the total sulphur of the coal or coke in the form of sulphur trioxide. The determination of the sulphur trioxide is made by fusing the ash obtained from the ignition of one gram of the sample with sodium carbonate and a few crystals of potassium nitrate. The fusion is transferred to a 12 cm. dish, hot water added, heat applied, and, when the fusion is disintegrated, 10 cc. of strong hydrochloric acid are added. The contents of the dish are evaporated to dryness, baked gently for 15 minutes, and, after cooling, the residue is moistened with hydrochloric acid (1-1). Hot water is then added, heat applied, and, when the soluble salts are dissolved, the silica is removed by filtration. The sulphur is precipitated and determined as previously described under the method for sulphur. The weight of barium sulphate, multiplied by the factor 34.27, furnishes the percentage of sulphur trioxide present in the ash.

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DETERMINATION OF PHOSPHORUS PENTOXIDE.

The percentage of phosphorus, as determined by the methods hereinbefore described, is multiplied by the factor 2.29 and the product represents the percentage of phosphorus pentoxide present in the ash.

DETERMINATION OF ALKALIES.

The ash from five to ten grams of the sample is ground in an agate mortar, with an equal weight of ammonium chloride and eight times its weight of calcium carbonate.

The finely comminuted and intimate mixture is transferred to a platinum crucible of 30 to 35 cc. capacity, and a slight covering of calcium carbonate is added. The covered crucible is protected by a suitable asbestos shield, so that only the lower two-fifths is subjected to the direct heat. A gentle heat is applied from a burner until the odor of ammonia is no longer apparent, when the bottom of the crucible is maintained at a bright red heat for three-quarters of an hour. The contents of the crucible are transferred to a platinum dish with the aid of hot water, about 100 cc. being added. The sintered cake is digested until disintegrated, and, if necessary, is crushed with a heavy glass rod. The residue is then removed by filtration, washed with hot water, and the filtrate received in another platinum dish. The filtrate is heated to the boiling point, and the lime is precipitated by adding a solution of one gram of ammonium carbonate, followed by 2 cc. of strong ammonia. The contents of the dish are boiled for 15 minutes, when the precipitate is removed by filtration and washed four times with hot water. The filtrate and washings are evaporated to dryness in a platinum dish. The dish and residue are carefully heated, and, when the ammonium salts are expelled, a few cc. of hot water are added, and the small amount of lime remaining in solution is separated by adding a few drops of a saturated solution of ammonium carbonate and 2 cc. of strong ammonia. The solution is then boiled for a few minutes, filtered, and the resulting filtrate is received in a platinum dish or crucible. The solution is evaporated to dryness and the crucible or dish is gently ignited. The residue is moistened with dilute hydrochloric acid (1-1), the solution is evaporated to dryness, and the contents of the crucible or dish are ignited at a dull red heat (approximately 400°C.) to constant weight. The residue is treated with hot water, the solution is filtered, and the filtrate retained in a small porcelain dish. The filter containing the slight insoluble residue is returned to the original crucible or dish which is again ignited and weighed. The difference in weight represents the combined weight of sodium and potassium chlorides.

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A blank determination should always be made, since, with the use of purest reagents, a positive result will always be obtained. This test should be made under the same conditions as described for the regular method and the result deducted from the combined weight of the chlorides. The separation of the alkalies is then made by either the direct or the indirect method.

DIRECT METHOD.

To the solution of the chlorides in the porcelain dish, an excess of platinic chloride is added, and evaporation is conducted until the solution solidifies on cooling. Twenty cc. of 80% alcohol are added. When the sodium salts are dissolved, the solution is filtered through a small filter, and the residue washed by decantation with alcohol of the same strength. Both dish and filter are freed from any residual alcohol by careful heating; the dish is cleansed with a minimum of hot water which is transferred to the filter and retained in a weighed crucible. The crucible is heated in an air bath to expel the water, with a gradual rise in temperature to a maximum of 135 degrees, which is maintained for fifteen minutes.

The crucible is then cooled and weighed, and the increase in weight, representing potassium platinic chloride, is multiplied by .1941, which yields the equivalent potassium oxide. The weight of potassium oxide, multiplied by 1.5830 is equivalent to grams potassium chloride, which, deducted from the combined weight of the chlorides, as previously noted, yields the weight of sodium chloride.

The weight of sodium chloride, multiplied by .5303, is equivalent to grams sodium oxide. The potassium and sodium oxides thus obtained are calculated to their respective percentage values.

INDIRECT METHOD.

To the solution of the chlorides, in a porcelain dish, 1 cc. of a 1% solution of potassium chromate is added as an indicator, and the chlorine is titrated with silver nitrate solution. A titration is also made in the same manner with the solution of the chlorides obtained in the blank, and the result deducted. The silver nitrate solution contains 4.791 grams silver nitrate crystals per liter, and 1 cc. is equivalent to 1 mg. chlorine. From these two results, the total chlorides and chlorine, the oxides of the alkalies may be calculated by the following formulae:

K_2O=2.925 x Chlorides—4.822 x Chlorine.

Na_2O=4.048 x Chlorine—1.925 x Chlorides.

The total Alkali Oxides=(Chlorides—.774 x Chlorine).

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ERROR OF DETERMINING ALKALIES BY THE INDIRECT METHOD.

The statement is often made that this method is only accurate when both alkalies are present to considerable extent. From the formula for potassium oxide (2.9254 x chlorides—4.822 x chlorine), it is readily seen that an error in determining the chlorine is magnified three and five times, respectively. Likewise in calculating the sodium oxide, we see that the error is magnified two and four times, respectively. In general then, an error of determination is multiplied in the calculation by a number less than five.

ULTIMATE ANALYSIS OF COAL.

CARBON AND HYDROGEN.

Experiments made with a small electric furnace of the type used for determination of carbon in steel have shown that fairly accurate results can be obtained with the use of this furnace for the determination of carbon and hydrogen in coal. The method of analysis is somewhat similar to that of a carbon determination in steel, but differs in that the coal sample is moved gradually into the hot part of the tube and the rate of flow of oxygen (300-400 cc. per minute) is greater. The standard method with the use of a gas furnace of 25 burners is recommended, however, as giving more nearly accurate results. The apparatus used for this determination in addition to the gas furnace is as follows:

Jena glass tube—length, 39", diameter, $\frac{5}{8}$"; purifying, drying and absorption bottles, tank of oxygen. The oxygen entering the combustion tube is purified and dried by means of a potash bottle and phosphoric anhydride tube, the carbon dioxide, generated by the combustion of the coal, is absorbed in a potash bottle of any type (the Vanier or Fleming bottle being preferred), while the generated water is absorbed in a phosphoric anhydride tube. The combustion tube is prepared in the following manner, starting at the exit end:

MATERIAL	LENGTH OF TUBE—INCHES
Empty	7
Plug Asbestos	1
Fused Lead Chromate	3
Plug Asbestos	1
Copper Oxide	15
Plug Asbestos	1
Empty	11

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The tube is first ignited and aspirated for 15 minutes. Blank determinations are then made until it is proven that the moisture and carbon dioxide are completely expelled from the apparatus, when the analysis is made in the following manner:

A portion of the tube is heated so that the copper oxide is red hot and the lead chromate a dull red, the absorption bottles are connected to the exit end of the tube and the combustion boat containing .2 to .5 gram of the sample is inserted to its proper position (near the asbestos plug). Purified and dried oxygen is then admitted at the rate of three bubbles per second, and the tube gradually heated by lighting one burner after another, starting at the entrance end. Care should be exercised that the temperature of the boat is not raised too rapidly, lest a portion of the volatile matter escape without being completely oxidized. When the volatile matter is completely expelled, the temperature is rapidly increased and the tube maintained at the highest temperature possible without danger of melting the glass. When the carbon is consumed, the tube is aspirated for five minutes, the absorption bottles are disconnected and weighed. The increase in weight, multiplied by the factor .1111 for hydrogen, and .2727 for carbon, gives the weight of these elements. This weight is calculated to percentage on the basis of weight of sample taken.

The residue in the boat should always be examined for unburned carbon and can then be weighed to determine the ash content of the coal.

NITROGEN.

One gram of the sample, pulverized to 100 mesh, is transferred to a Kjeldahl flask containing .7 gram of mercury and 7 grams of potassium sulphate. Then 30 cc. of strong sulphuric acid are added. A gentle heat is applied until frothing ceases, when the temperature is gradually increased until the contents of the flask boil gently. The flask is maintained at this temperature until the solution is colorless and heating is continued for an additional two hours with an occasional addition of a few crystals of potassium permanganate. The flask and contents are allowed to cool, approximately 250 cc. of water are carefully added, followed by a small piece of paraffine to prevent frothing, and a few pieces of zinc to prevent bumping.

The flask is connected with a condenser, and approximately 50 cc. of caustic soda solution (50%), containing three grams of sodium sulphide are added. The sulphide is added to precipitate the dissolved mercury. The end of the condenser is connected by rubber tubing to an adapter, which

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dips into a 250 cc. Erlenmeyer flask containing 20 cc. of N/10 sulphuric acid. Heat is applied and the contents of the flask boiled until 150 cc. of solution are condensed.

The adapter is then disconnected and washed with water, the washings being retained in the flask. The acid solution is titrated with N/10 caustic soda solution, using methyl orange as an indicator. Each cc. of N/10 acid, neutralized by ammonia, is equivalent to .14% of nitrogen. A blank determination should always be made as an actual determination, and a correction, if necessary, should be applied.

ASH, SULPHUR, OXYGEN.

The ash is determined preferably according to the method previously described under determination of ash, or by weighing the residue in the boat after the determination of the hydrogen and carbon.

Sulphur is determined by the method previously described.

Oxygen is obtained by subtracting the sum of the carbon, hydrogen, sulphur, nitrogen, and ash from 100.

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METHODS FOR THE DETERMINATION OF THE CALORIFIC VALUE OF FUELS.

The calorific value of a fuel represents its heating value per unit of substance burned. For practical purposes, two units are used, the Kilogram calorie (Cal.) and the British thermal unit (B. t. u.). A Cal. represents the quantity of heat necessary to raise the temperature of one Kilo. of water through 1° C. at 15° C., while a B. t. u. represents the quantity of heat necessary to raise the temperature of one pound of water through 1° F. at 60° F. One Cal. is thus 3.97 B. t. u. as is shown by the following calculation in which 2.2046 represents the ratio of pound to Kilo. and 1.8 represents the ratio of 1° C. to 1° F.

$$\text{Cal.} = 1.8 \times 2.2046 = 3.97 \text{ B. t. u.}$$

The calorific value of fuel is reported as B. t. u. per pound or Cal. per Kilo. To convert a B. t. u. per pound to a Cal. per Kilo., it is only necessary to divide the B. t. u. by 1.8, as the heat developed by the combustion of a unit weight of fuel is always measured by the rise in temperature produced in the same unit weight of water. Since it is thus a simple matter to convert B. t. u. per pound to Cal. per Kilo., and since the B. t. u. is used almost exclusively throughout the U. S. Steel Corporation, this unit only will be referred to in the following methods.

It is the general practice to report the total thermal value of a fuel, i. e., the gross B. t. u. per pound, as determined on a sample dried at 105° C. The net B. t. u. takes into consideration the heat of vaporization of the water generated from the combustion of the hydrogen. This value is subtracted from the gross in calculating the net B. t. u.

The gross B. t. u. on a wet sample is calculated by applying the following equation:

$$\text{B. t. u. value (wet sample)} = \text{B. t. u. value (dry sample)} \times \frac{(1 - \%\ \text{Moisture})}{100}$$

The gross B. t. u. on a wet sample, however, does not represent the calorific value of a fuel "as fired," since, in order to vaporize the moisture, a definite amount of heat will be lost.

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The net B. t. u. on a wet sample can be calculated from the gross B. t. u on a dry sample by the following equation:

$$\text{Net B. t. u. (wet sample)} = \text{gross B. t. u. (dry sample)} - \left[\frac{M}{100} \times \text{gross B. t. u. dried sample} + \left\{9 \times \frac{H}{100} \times \frac{(1-M)}{100} + \frac{M}{100}\right\} 1056.7\right]$$

H=Hydrogen.

M=Moisture.

1056.7=Latent heat of vaporization of uncondensed steam at 62° F. (Marks and Davis).

That the loss in heating value, due to the moisture and generated water, is appreciable is shown by the following calculation, in which it is assumed that a fuel has a moisture and hydrogen content of 4 and 5 per cent., respectively, and a gross B. t. u. value of 14200—dried sample.

$$14200 - (.04 \times 14200) - (9 \times .048 + .04)\ 1056.7 = 13133 \text{ B. t. u.}$$

The net B. t. u. value of the wet fuel in this case would be 1067 B. t. u. less than the gross value on a dry sample. It is thus apparent that the calorific value as usually reported is misleading, and it would, therefore, seem as if a more practical method would be to report also that value which a fuel possesses when in its natural state, i. e., the net B. t. u. on a wet sample.

For the direct determination of the calorific value of a fuel, two methods are recommended—those involving the use of the oxygen and of the sodium peroxide bomb calorimeters; while for calculation, Dulong's formula, requiring an ultimate analysis, is recommended, although the method for deriving a formula from the proximate analysis is also given.

DIRECT DETERMINATION BY MEANS OF THE OXYGEN OR THE SODIUM PEROXIDE BOMB CALORIMETER.

For the direct determination of the calorific value of a fuel, the oxygen bomb method is recommended as giving results most nearly accurate. The sodium peroxide calorimeter will give results that are sufficiently accurate for practical purposes. Its initial cost is less than the former and it is simpler to operate.

There are a number of standard types of calorimeters, both oxygen and sodium peroxide bomb and it is, therefore, not proposed to specify a particular make of apparatus. However, in all cases, it is highly important that the thermometer used be carefully calibrated and that the apparatus be

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standardized with the use of C. P. benzoic acid, napthalene or cane sugar. Such standardization should be made under conditions similar to an actual determination, and the correction as found should always be applied.

Since the sample used in a calorimeter is dried at a temperature of 105° C., and the moisture formed by the combustion of the hydrogen is condensed, the result thus obtained represents the gross B. t. u. on a dry sample. To obtain the net B. t. u., it is essential that the percentage of hydrogen be known. This is determined by an ultimate analysis; however, it is possible to calculate it to a fair degree of accuracy from the proximate analysis. Two formulas for this purpose are given. In calculating the hydrogen from these formulas, it will be found that, for certain grades of coal, one will give better results than the other, and it is thus recommended that each operator prove these formulas for the different grades of coal at his plant, and select the one that is more suitable.

Formula of Seyler.

% Hydrogen=1.72+2.43 (Log V. M.).

V. M.=Volatile Matter on ash free, dry coal.

Formula of Diederich.

$$\% \text{ Hydrogen} = \text{V. M.} \left\{ \frac{7.35}{\text{V. M.} + 10} - .013 \right\}$$

To correct the calorimeter result to the net B. t. u. on a wet basis, the formula, hereinbefore described, should be applied.

OXYGEN BOMB CALORIMETER.

APPARATUS.

The outfit consists of a platinum or porcelain enamel steel bomb, platinum terminals and combustion tray, motor-driven screw stirrer, brass bucket, double walled calorimeter jacket, oxygen tank, pressure gage, thermometers and battery of dry cells, as shown in the accompanying photograph.

Ordinary thermometers, graduated in 1° C., are used for taking temperature of room and calorimeter jacket. For the calorimeter, a Standard Beckmann thermometer, scale range 6° C., graduated in .01° and certified by the U. S. Bureau of Standards, is recommended.

STANDARDIZATION.

The water equivalent of the calorimeter is determined by a series of

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OXYGEN BOOM CALORIMETER

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combustions of Standard samples of benzoic acid, naphthalene or sugar (preferably benzoic acid), performed under exactly the same conditions as for the coal combustions.

THE DETERMINATION.

The calorimeter jacket is filled with water adjusted to about 2° above the temperature at which the thermometer is set. A 1-gram sample of the coal, dried and pulverized to pass a 60 mesh sieve, is placed in the platinum combustion tray. The platinum terminals are connected by wrapping iron wire (about No. 34 B. & S. gage) around the ends so as to form a loop in contact with coal. The amount of wire used (about 5 cm.—weight about 8 mgs.) is measured for each determination and the weight determined from time to time. Five cc. of water are added to the bomb, the top screwed down tightly and oxygen admitted slowly until the gage shows 20 to 30 atmospheres in the bomb. The bomb is placed in the bucket within the calorimeter jacket, which contains the required amount of water (2300 to 2400 grams).

The temperature of the water for the calorimeter bucket is adjusted to about 2° below jacket temperature and measured in a calibrated Florence flask. The cover is replaced, the stirrer connected and the thermometer adjusted so that it is submerged to zero point and the bulb is not in contact with any metallic parts of the apparatus.

The stirrer is started and, after two minutes, thermometer readings are taken at 1-minute intervals for five minutes, or until the rate of change per minute is nearly constant. The thermometer readings are taken by means of a telescope, or a movable magnifier attached to the thermometer, interpolating to 0.001° C. The current is turned on for about one-half second and thermometer readings taken at one-half minute intervals for the next minute, and then at minute intervals until five or six readings show uniform rate of fall. The thermometer should always be lightly tapped before readings are taken. The stirrer is run at a uniform rate throughout the determination and rapid enough to insure mixing. After the combustion, the gas is carefully released, the bomb opened and examined for unburned material. If the combustion appears complete, the bomb is thoroughly washed out with distilled water, and the washings titrated with standard sodium carbonate solution (1 cc.=.02173 nitric acid=5 calories) using methyl orange as an indicator.

The figures given below and taken from an actual determination show the method of calculating the result and the corrections made. In order to

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convert the thermal value of the coal to B. t. u.'s, the calories are multiplied by 1.8. The product thus obtained will represent the gross thermal value of the coal on a dry sample; to obtain the net B. t. u.'s on a wet sample, the formula previously described should be applied.

Moisture=.80%
Sulphur =.60%

Time A. M.		Readings ° C.			
8.55		.902 Lower Reading	.9320	Upper Reading.....	3.6590
		Certificate Correction	.0066	Certificate Correction..	.0217
			.9386		3.6807
8.57		.913 Rate of change in prelimi-			.9386
		nary periods		Temperature change...	2.7421
		+.0060		Setting Factor.....	.0033
8.58		.920		Radiation Loss.....	.0091
9.00		.932+.0060		Stem Correction.....	.0035
					2.7580
			+.0023		
				Water equivalent.....	.2831
.82	9.00—½	1.750+.0034	+.0031	Total heat (calories)...	7808
			+.0008	Correction for wire, acid, and sulphur in calories	42
1.10	9.01	2.850—.0002			
			—.0013	Heat derived by Comb.	7766
.69	9.02	3.540—.0024		Dry Basis.....	7828
			—.0025		
.10	9.03	3.640—.0027			
			—.0028		
.02	9.04	3.658—.0028			
			—.0028	Wire Burned (1.7 Cal. per mg.)= 8.2 mg.....=14.0 Cal.	

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TIME A. M.	READINGS ° C.		
9.05	3.659—.0028		Titer (1 cc.=5 Cal.) 4.1 cc.....=20.5 Cal.
		—.0028	Sulphur (.01 gm.= 13 Cal.) .0060..= 7.8 "
			42.3
9.06	3.659—.0028	—.0122	
		—.0091	
9.07	3.654		
9.08	3.652		
9.09	3.650		
9.10	3.647	Rate of change in final period—.0028	
9.11	3.643		
9.12	3.640		

Setting 24° C.
Room Temperature 20° C.

THE CORRECTIONS.

The corrections for calibration, emergent stem and setting factor are made according to certificate furnished by the Bureau of Standards.

RADIATION.

The rates of change for the first and last periods are from +.0060° to —.0028°.

The change in rate per degree of temperature change in the combustion period is, therefore, .0060°—(—.0028°)=.0088° divided by the total rise 2.74°=.0032°.

The change in temperature for the first half minute of the combustion period is .82°, and .82°×.0032°=.0026°, the change in rate during first half minute of combustion period. Then, .0060°—.0026°, represents the rate of temperature change at readings at 9.00—½ A. M.

The rate of change for the other readings of the combustion period is calculated in the same manner.

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The temperature correction for the heat loss or gain for each of the different intervals is found by adding the rates at the beginning and end of the interval, and dividing by 4 for half-minute interval and by 2 for minute interval.

The observed temperature is corrected for heat gain or loss. In this example, the loss amounts to .0091°, which is added to the observed temperature rise.

ACIDITY.

The acidity of the washing is due to the oxidation of both nitrogen and sulphur. The heat, generated by the oxidation of nitrogen to aqueous nitric acid is taken as 230 calories per gram of acid formed, or 5 calories per cc. of soda solution used. A further correction is necessary for the excess of heat of combustion of the sulphur to aqueous sulphuric acid in the bomb over sulphur to sulphur dioxide in the air, and for the excess of heat of formation of the sulphuric acid titrated as nitric acid. The difference in heat of formation of aqueous sulphuric acid and sulphur dioxide (4450 Cal. —2250 Cal.) is 2200 calories. In titrating the bomb washings, 126 parts of nitric acid are equivalent to 98 parts sulphuric acid, or 32 parts sulphur; hence 1 cc. of soda solution=.0055 gm. S.=12.1 calories, a difference of 7.1 calories. This difference of 7.1 calories divided by .0055 gm. S. (value of 1 cc. soda solution)=1276 calories or 13 calories per .01 gm. S.

Total correction for acidity equals the total cc. of soda solution×5 (the factor for nitric acid)+the centigram of sulphur of the coal×13. This amount, with the heat of combustion of iron wire, is subtracted from the total calories found. A sample for moisture is weighed at the same time as for combustion and the results calculated on the basis of dry coal.

SOLUTION REQUIRED.

Sodium Carbonate Solution.

Sodium Carbonate	18.28 grams.
Water	1000 cc.

SODIUM PEROXIDE BOMB CALORIMETER.

APPARATUS.

The outfit consists of an inner and outer calorimeter jacket, brass bucket and bomb support, bomb provided with paddles, shaft provided with pulley, thermometer and motor for stirring.

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DETERMINATION.

One-half to one gram of accelerator is transferred to the bomb and one-half gram of coal or coke, powdered to 100 mesh, is added. The contents of the bomb are thoroughly mixed by stirring with a glass rod or by shaking. The proper quantity of sodium peroxide is added and the whole thoroughly mixed by vigorous shaking.

The bucket is filled with two litres of water adjusted to 1 or 2° C. below room temperature, and is then set upon its support. The bucket and contents are placed within the calorimeter jacket, the lid adjusted, and the bomb is revolved at a rate of approximately 150 R. P. M. After stirring for a few minutes, thermometer readings are taken each minute for several minutes, when the charge is ignited either by an electric current or with a hot slug. Temperature readings are taken every minute for 9 or 10 minutes. The thermometer should be lightly tapped before taking readings.

The following figures, taken from an actual determination, show the manner in which readings are recorded and results calculated:

MINUTES.	TEMPERATURE.	
1	2.128° C.	
2	.142	
3	.138	
4	.142 ignition.	
5	3.580	
6	4.500	
7	.755	
8	.770	
9	.772 Maximum	
10	.766.....	.006
11	.762.....	.004
12	.761.....	.001
13	.758.....	.003
		.014

Maximum Temperature.....	4.772
Ignition Temperature.....	2.142
	2.630

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Radiation Loss	.014
	2.644
Correction for fuel, ash, accel., etc	.189
	2.455

B. t. u. equals 2.455×3117×1.8.

RADIATION.

The drop in temperature per minute after the maximum temperature has been reached shows the correction to be added to each minute preceding the maximum, with the exception of the minute immediately following the ignition.

CORRECTIONS.

Corrections should be applied for the sulphur and ash content of the fuel, the hydration factor, and for the fuse wire or hot slug, according to the directions accompanying the apparatus.

THERMAL VALUE CALCULATED FROM ULTIMATE ANALYSIS.

The calorific value of a fuel can be calculated from Dulong's formula, given below. Although the combination of elements in coal is not definitely known, and the calculation is made as though they existed in the free state, nevertheless the application of this formula to the ultimate analysis gives results which will agree very well with those obtained with the use of a calorimeter.

DULONG'S FORMULA.

$$\text{B. t. u. per pound} = 14544\,C + 62028\left\{H - \frac{O}{8}\right\} + 4050\,S.$$

C=Carbon. O=Oxygen.
H=Hydrogen. S=Sulphur.

THERMAL VALUE CALCULATED FROM PROXIMATE ANALYSIS.

Of the many formulas devised for the calculation of the calorific value of a fuel from the proximate analysis, a careful study of those best known has shown that none will give results that are reliable for all kinds of coal. Practically all will give results that are dependable for certain coals, but fail in others which have a materially different composition. The only formula that has proven satisfactory is that one in which a variable factor is established

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by the operator for each kind of coal, based on an ash free, dry sample. If constant conditions are maintained, results sufficiently accurate for technical purposes will be given. This factor for a certain coal is an average calculated from many calorimeter determinations, and is obtained by applying to these results the following formula:

$$\text{Factor (dry coal)} = \frac{\text{Calorimeter Result B. t. u.}}{1 - \frac{\%\ \text{Ash}}{100}}$$

After the average factor has been established, the calorific value of an unknown coal is calculated according to the following formula:

$$\text{B. t. u. (Unknown Coal)} = \text{Average Factor} \times 1 - \frac{\%\ \text{Ash}}{100}$$

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SAMPLING AND ANALYSIS OF BY-PRODUCTS.

AMMONIA PRODUCTS.

AMMONIA LIQUORS AND STILL WASTE.

Sampling.

Concentrated Ammonia Liquor is usually contained in tanks and cars and is sampled by means of a gallon bottle attached to a long rod. The bottle is carefully lowered and raised from top to bottom of the ammonia liquor at such a uniform rate that it is not quite filled when it reaches the surface. The bottle is then stoppered, taken to the laboratory, well shaken, and six one pint bottles are filled with the liquor. Three of these are used for analysis, two sent to the purchaser and the remaining one is reserved for future reference.

Weak Liquor contained in tanks is sampled as the concentrated liquor just described. The liquor from scrubbers may be sampled continuously or intermittently by inserting a pipe in the upper section of the scrubber and collecting the sample in a bottle, while the liquor in the bottom of the scrubber may be sampled by lowering a bottle in the overflow or seal pipe, as described under "Concentrated Liquor."

Still Waste is sampled by withdrawing 500 to 1000 cc. from the waste main.

Specific Gravity.

This test is usually made on the concentrated liquor only. One of the pint bottles containing the sample is cooled slightly below 15° C.; the liquor is then allowed to stand until it reaches a temperature of just 15.5° C The specific gravity is determined by means of a hydrometer after the sample has been transferred to a tall cylinder or other suitable vessel.

Free Ammonia.

For the determination, 50 cc. of weak liquor are used, but only 5 cc. of concentrated liquor, which is obtained in the following manner: 50 cc. of the concentrated liquor at 15.5° C. are transferred by means of a pipette to a 500 cc. volumetric flask, containing approximately 350 cc. of cold distilled water, taking care to hold the tip of the pipette slightly below the surface of the water. The flask is then filled to the mark and the contents are well mixed. Fifty cc. of this diluted solution, representing 5 cc. of the concentrated liquor, are used for the determination. The sample is transferred to a flask, diluted to a volume of approximately 200 cc. and titrated with normal sulphuric acid, using methyl orange as an indicator.

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Free ammonia is reported as per cent. by weight in concentrated liquor and as grams per litre in the weak liquor. The equations for these calculations are as follows:

$$\%\text{ of Free Ammonia (Concentrated Liquor)} = \frac{\text{cc. Sulphuric Acid} \times 1.7}{5 \times \text{sp. gr. of Liquor}}$$

G. P. L. of Free Ammonia (Weak Liquor) = cc. Sulphuric Acid $\times .017 \times 20$.

TOTAL AMMONIA.

This determination is made with the use of a distillation apparatus. The flask used is of one litre capacity, round, with flat bottom and short neck, and is connected to the condenser preferably by a Kjeldahl distilling head. The receiver for the distillate is a 500 cc. round flask with flat bottom. Fifty cc. of the diluted solution of the concentrated liquor (equivalent to 5 cc. concentrated liquor), 50 cc. of weak liquor, or 500 cc. of still waste, are transferred to a distillation flask and diluted, if necessary, to a volume of 500 cc. Twenty cc. of 10% caustic soda solution are added, the contents of the flask heated, and the distillate collected for 30 minutes after boiling has started. The distillate is received in a flask containing 65 cc. of normal sulphuric acid. When the distillation is completed, the excess acid is titrated with normal caustic soda solution, using methyl orange as an indicator. The total ammonia is reported in the same manner as the free ammonia, i. e., in concentrated liquor as per cent. by weight, and in the weak liquor and still waste as grams per litre. The calculation is made by applying the formulas given under free ammonia, the cc. of sulphuric acid representing the volume of acid neutralized by ammonia.

FIXED AMMONIA.

The difference obtained by subtracting the free ammonia from the total ammonia represents the fixed ammonia.

SULPHUR.

Total Sulphur is usually determined in the concentrated liquor. Five cc. of the diluted solution of the concentrated liquor (equivalent to .5 cc. of concentrated liquor) are transferred to a beaker containing about 50 cc. of water. Two cc. of saturated bromine water are added, the solution is boiled for about five minutes, and then slightly acidified with hydrochloric acid. Any insoluble organic matter is removed by filtration, the filtrate is again treated with bromine water, boiled for five minutes and refiltered, if necessary. The sulphur is precipitated and determined as described under determination of sulphur in coal and coke.

Sulphur Existing as Sulphate is usually determined in the concentrated liquor. Five cc. of the diluted solution of the concentrated liquor are

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evaporated just to dryness in a beaker. Fifteen cc. of water are added, the contents of the beaker boiled, and the insoluble organic matter removed by filtration. The solution is slightly acidified with hydrochloric acid, and the sulphur determined by precipitating with barium chloride, as described under the "Determination of Sulphur in Coal and Coke."

Sulphur Existing as Sulphide is usually determined in the weak liquor. Ten cc. of the weak liquor are transferred to a beaker containing 200 cc. of water, 10 cc. of hydrochloric acid (1-1) and 10 cc. of starch solution are added. The contents of the beaker are gently stirred, and N/10 iodine solution added from a burette in successive portions, followed by stirring until the blue color begins to fade slowly. At this point the iodine solution is cautiously added until a final drop yields a permanent blue color that does not fade upon continued stirring. The result is reported as grams of hydrogen sulphide per litre and is calculated according to the following formula:

Grams per litre of hydrogen sulphide=cc. of iodine solution×.0017×100.

PYRIDINE.

One hundred cc. of concentrated liquor are transferred to a litre flask containing about 150 cc. of water. Methyl orange is added, and the solution is just acidified with sulphuric acid (1-3), care being taken to keep the contents of the flask cool in order to prevent loss of pyridine. Normal caustic soda solution is added to the flask until the solution is neutral, when an excess of 5 cc. are added. The contents of the flask are then distilled in the following manner: A litre bottle with wide mouth, containing 100 cc. of sodium hypobromite, is fitted with a two hole rubber stopper. Through one of the holes is placed a delivery tube reaching almost to the bottom of the bottle and connected to the distilling flask; the other hole is fitted with a short stem delivery tube which is connected to a flask containing 50 cc. N/10 sulphuric acid. The distilling flask is heated, and the pyridine and ammonia are driven over by the generated steam into the bottle. The pyridine passes through and is absorbed in the flask by the N/10 acid, while the ammonia is oxidized by the hypobromite. When the distillation is completed, the excess N/10 acid is titrated with N/10 caustic soda solution, using methyl orange as an indicator, and the percentage of pyridine is calculated according to the following equation:

$$\frac{\text{cc. of acid neutralized by pyridine} \times .0079}{100 \times \text{specific gravity of liquor}} = \text{per cent. of pyridine.}$$

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FREE LIME.

For the determination of free or active lime in the still waste, two methods are given, the first of which is recommended as giving results that will indicate more closely those obtained in actual practice.

Distillation Method. Two hundred cc. of still waste are transferred to a distilling flask containing 300 cc. of water. The contents of the flask are boiled until about 200 cc. remain, cooled, and 300 cc. of water and 10 grams of crystallized ammonium chloride are added. Twenty-five cc. of N/2 sulphuric acid are placed in the receiver, and the solution is distilled until the lime has dissolved. When 250 cc. of distillate have been condensed, the excess acid is titrated with N/2 caustic soda solution, and the cc. of acid neutralized by the ammonia is calculated to grams per litre of lime, according to the following equation:

G. P. L. free lime=cc. of acid×.014×5.

Direct Titration. Two hundred cc. of waste liquor are transferred to a beaker and boiled until the ammonia has been completely expelled. The solution is then cooled and titrated with N/2 nitric acid, using phenolphthalein as an indicator. The free lime is calculated as specified in the preceding method.

CHLORIDES IN WEAK LIQUOR.

The fixed ammonium salts in weak liquor consist principally of the chloride. However, a small amount of sulphate, and usually traces of cyanides and sulphocyanates are present. If the last two acids are present in very small amounts, a direct determination of chlorides can be made by the usual methods; if they are present in appreciable amounts, however, special precautions must be taken and the determination in this case is made as follows:

One hundred cc. of weak liquor are transferred to a No. 2 beaker and boiled until the free ammonia is completely expelled. The solution is then cooled, transferred to a graduated flask of 100 cc. capacity, and diluted to the mark. Twenty cc. of this solution are transferred to a small flask and boiled with frequent additions of hydrogen peroxide (3% solution freshly prepared from pure, acid free hydrogen peroxide), whereby the cyanide compounds are oxidized. When completely oxidized, the brown color of the solution will disappear. Ten to 15 drops of potassium bichromate solution are then added and the solution boiled for five minutes to destroy the excess of hydrogen peroxide.

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Approximately two hours are required to oxidize the solution. Should the organic matter resist oxidation, further additions of peroxide must be made and the boiling continued with addition of potassium bichromate, as previously described. When completely oxidized, the solution is cooled and made slightly alkaline with sodium bicarbonate. Alkalinity of the solution is indicated by its color changing to a greenish yellow tint. The solution is then titrated with N/10 silver nitrate solution, as an ordinary chloride titration. The grams of chlorine per litre of liquor are calculated according to the following equation:

Chlorine, grams per litre=.00355×50×cc. N/10 silver nitrate.

A blank determination should always be made as an actual determination, and the necessary correction applied.

SATURATOR LIQUOR.

Free Sulphuric Acid.

Ten cc. of the sample are transferred to a beaker containing 50 cc. of water. The acid is then titrated with normal caustic soda solution, using methyl orange as an indicator.

cc. normal caustic soda×4.9=G. P. L. acid.

Solutions Required.

Normal and Fractional Normal Acid and Alkali Solutions. The chemicals most commonly used as the basis for the preparation of standard acid and alkali solutions are sodium carbonate and sulphuric acid. Both of these have disadvantages, as much time is consumed in preparing a normal sulphuric acid solution, and sodium carbonate, aside from being very hygroscopic, is difficult to obtain in a pure state. As a basis for the standardization of acid and alkali solutions, C. P. benzoic acid has a number of advantages; it can be obtained pure, little time is consumed in making a determination, after being fused it is but slightly hygroscopic, and the error in weighing is negligible, as the ratio of the molecular weight of the acid radicle to the total molecular weight is very small. It is, therefore, recommended that C. P. benzoic acid be used as the basis for the preparation of all normal acid and alkali solutions.

In the methods of analysis requiring the use of normal alkali, caustic soda solution has been specified only for the sake of convenience in describing the methods. Normal sodium carbonate solution can be used just as well, and the use of either is optional.

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Normal Caustic Soda Solution.

Caustic Soda	40.05 grams.
Water	1000 cc.

As caustic soda contains traces of sodium carbonate, the solution is treated with 10 cc. of a saturated solution of barium hydrate. The barium carbonate and any other precipitated impurities are removed by filtration after settling.

The solution is standardized with the use of fused benzoic acid. The benzoic acid is transferred to a platinum crucible, heated to its melting point, and maintained at a temperature of 130°–135° C., for one to two minutes, or until completely fused. The crucible is then removed from the heat and rotated so that the fused acid solidifies along the sides of the crucible. When cold, the acid is easily removed by gently pressing the crucible. For the standardization of normal caustic soda solution, 3.0512 grams of fused benzoic acid are transferred to a glass-stoppered Erlenmeyer flask and dissolved in 50 cc. of neutral alcohol (95%). This solution is titrated with the caustic soda solution, using phenolphthalein as an indicator. Exactly 25 cc. of normal caustic soda solution are required to neutralize the specified weight of benzoic acid.

Normal Sodium Carbonate Solution.

Sodium Carbonate	53.05 grams.
Water	1000 cc.

The solution is adjusted so that 1 cc. is equivalent to 1 cc. of normal sulphuric acid, using methyl orange as an indicator.

In using methyl orange, a blank determination should always be made, and a correction applied if necessary.

Fractional Normal Alkali Solutions.

These are prepared as the normal solutions just described. by using fractional weights of the reagents.

Normal Sulphuric Acid.

Sulphuric Acid (1.84 sp. gr.)	29.2 cc.
Water	1000 cc.

The acid is adjusted so that 1 cc. is equivalent to 1 cc. of normal caustic soda solution, using phenolphthalein as an indicator.

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Fractional Normal Acid Solutions.

These are prepared as the normal solution just described—by using fractional weights of the reagent.

Tenth Normal Iodine.

Potassium Iodide	28.00 grams.
Iodine (Resublimed)	12.70 grams.
Water	1000 cc.

The iodine and potassium iodide are transferred to a graduated, one litre flask, 25 cc. of cold water added, and the flask shaken until the iodine has dissolved. The solution is diluted to one litre. A blank determination should always be made as an actual determination, and a correction applied.

Starch Solution.

Starch (Soluble)	6.0 grams.
Water	1000 cc.
Zinc Chloride (as preservative)	5.0 grams.

The starch is mixed with a little cold water (25 to 50 cc.), and the paste is added to one litre of water heated nearly to the boiling point. The zinc chloride, dissolved in 10—15 cc. of water, is added after the solution has cooled.

Sodium Hypobromite Solution.

Caustic Soda	100 grams.
Bromine	25 cc.
Water	1000 cc.

The caustic soda is dissolved in the water and, after cooling, the bromine is cautiously added.

Phenolphthalein Solution.

Phenolphthalein	1 gram.
Ethyl Alcohol	1000 cc.

Methyl Orange Solution.

Methyl Orange	1 gram.
Water	1000 cc.

Tenth Normal Silver Nitrate.

Silver Nitrate	17 grams.
Water	1000 cc.

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AMMONIUM SULPHATE.

Sampling.

Ammonium sulphate is sampled either when in a stock pile or as it is being loaded into cars for shipment. In the latter case the sample is obtained by taking a small scoopful from each bag or wheelbarrow. The individual samples, representing a car, are combined, crushed, mixed, and quartered until about two pounds remain. Four 8 oz. bottles are filled with the remaining sample, two of which are used for analysis and the other two are saved for future reference.

Ammonium sulphate in a stock pile is sampled similar to a soft or hard ore, as is described on page 16, United States Steel Corporation Methods for the Commercial Sampling and Analysis of Iron Ore. The sample is prepared for analysis by crushing, quartering, etc., as the car sample previously described.

Moisture.

Ten grams of the sample are transferred to a porcelain dish and heated in an air bath at a temperature of 105° C. for one hour. The dish and contents are then cooled in a desiccator and weighed. The loss in weight represents moisture.

Free Acid.

Twenty-five grams of the salt are dissolved in 100 cc. of cold water and titrated with normal caustic soda solution, using methyl orange as an indicator.

$$\% \text{ Free Sulphuric Acid} = \frac{\text{cc. of caustic soda} \times .049 \times 100}{25}$$

Total Ammonia.

Five grams of the sample are dissolved in 200 cc. of water, and the ammonia is determined by distillation as the fixed ammonia in liquors previously described.

ANALYSIS OF CRUDE SULPHURIC ACID.

Sampling.

The sample is obtained with the use of a quart bottle attached to a long rod—as described under Sampling of Concentrated Ammonia Liquor.

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SPECIFIC GRAVITY.

The specific gravity is determined by means of a hydrometer. The reading is corrected to 60° F., and the percentage of acid is interpolated with the use of Ferguson and Talbot tables, which are found in a number of standard chemical works, and may be obtained in convenient form from the Manufacturing Chemists Association of the United States, Exchange Building, Boston, Mass.

ACID CONTENT.

Approximately 2 cc. of the sample are transferred to a tared bottle and weighed. The bottle and contents are then placed in a beaker containing 200 cc. of water, and the acid is titrated with normal caustic soda solution, using methyl orange as an indicator. The percentage of acid is calculated by the following equation:

$$\% \text{ of acid} = \frac{\text{cc. caustic soda} \times .049 \times 100}{\text{weight of acid used}}$$

ARSENIC.

DIRECT REDUCTION METHOD.

Fifty grams of the acid are transferred to a litre flask containing 600 cc. of water, and approximately 5 grams of sodium sulphite are added. The contents of the flask are boiled until the volume of the solution has been reduced to 100 cc. The arsenic can either be determined by a direct titration of this solution with N/10 iodine, or it can be precipitated as the sulphide, removed by filtration, dissolved and then titrated. In the former case, the solution is cooled, just neutralized with sodium carbonate, and 5 grams of sodium bicarbonate are added. This solution is diluted to a volume of approximately 600 cc. and the arsenic determined by titrating with N/10 iodine solution. In the latter case, hydrogen sulphide is passed through the solution until the arsenic is completely precipitated. The precipitate is removed by filtration, using a Gooch crucible, washed six times with water, and then transferred to a No. 2 beaker. Fifty cc. of pure sulphuric acid are added, the contents of the beaker boiled until the precipitate is dissolved and the generated hydrogen sulphide expelled. This solution is just neutralized with sodium carbonate, 5 grams of sodium bicarbonate are added and the arsenic determined after dilution by titration, as described above.

The iodine solution is prepared as previously described under "Solutions Required." It is essential that a blank determination be made as an actual determination, and the necessary correction applied. One cc. of N/10 iodine solution equals .00495 grams of arsenious oxide.

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DISTILLATION METHOD.

The apparatus used for this determination (see print) consists of a 250 cc. flask closed with a 2 hole rubber stopper; through one of the holes is inserted a thistle tube or separatory funnel provided with a glass stopcock; through the other hole is inserted a bulb tube, bent at a right angle. A 50 cc. pipette serves as a delivery tube. It is connected at one end by rubber tubing to the bulb tube, and the other end dips into a test tube (10" x 1"), filled to approximately three-fourths of its capacity with water. The test tube is surrounded with cold water contained in a beaker.

The determination is made by adding 25 cc. of hydrochloric acid (1.19 sp. gr.) to the flask through the thistle tube. The flask is then placed over a small flame of an Argand burner, and 25 cc. of the sample are added to the flask, from a graduate, a few drops at a time. The stop cock should be kept open in order to prevent back pressure. The graduate is washed three times with 10 cc. of hydrochloric acid (1.19 sp. gr.), and the washings are transferred to the flask. The stop cock is then closed and the contents of the flask heated until the pipette becomes hot. The contents of the test tube are transferred to a beaker, neutralized with sodium carbonate and 5 grams of bicarbonate are added, and arsenic determined by titration—as described in the previous method.

ANALYSIS OF LIME.

SAMPLING.

A car is sampled by the parallel system. The first line is located along the median line of the car; the other two lines are about two-thirds the distance from this line to the sides of the car. There should be at least 24 sampling points which are arranged symmetrically along these lines, the sample being taken by means of a scoop having a capacity of approximately one pound.

The sample is prepared by crushing and quartering alternately, until approximately 50 grams of 1/10" size remain. This sample is then pulverized in an iron mortar until reduced to pass a 60 mesh sieve.

ACTIVE LIME.

Since lime, in the recovery of by-products, is used only to displace ammonia in fixed ammonium compounds, a complete analysis is seldom made. The essential determination is that of free or active lime, which is made by the distillation or direct titration method.

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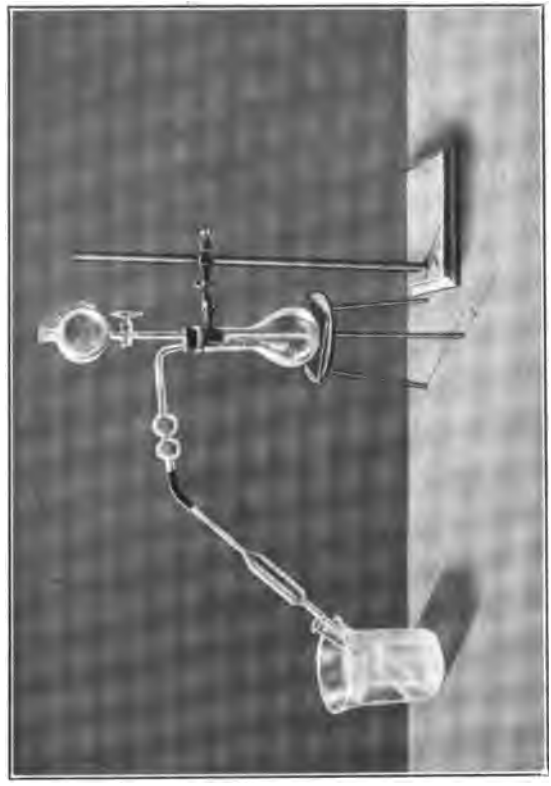

APPARATUS FOR DETERMINATION OF ARSENIC.

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DISTILLATION METHOD.

One gram of the sample is transferred to a distillation flask, and 500 cc. of water and 5 grams of ammonium chloride are added. The ammonia is distilled in the usual manner, and is received in a flask containing 40 cc. of normal sulphuric acid. The distillation is conducted slowly, allowing time for the reaction between the lime and ammonium chloride to be completed. When 300 cc. of distillate have been collected, the apparatus is disconnected, the excess sulphuric acid titrated with normal caustic soda, and the volume of acid neutralized by ammonia is calculated to percentage of free lime, according to the following equation:

cc. sulphuric acid $\times 2.8 =$ % active lime.

In samples containing magnesia, this method will give results showing a higher percentage of lime than the actual content, however, this value will indicate more closely results obtained in actual practice.

DIRECT TITRATION METHOD.

One gram of the sample is transferred to a 500 cc. Florence flask containing 250 cc. of water which has been boiled to remove carbon dioxide. The flask is then stoppered with a Bunsen valve and its contents boiled for five minutes. The flask and contents are cooled, and the solution titrated with normal nitric acid, using phenolphthalein as an indicator. The number of cc. of acid required to discharge the pink tint of the indicator are calculated to percentage of lime, according to the following equation:

cc. of acid $\times 2.8 =$ % active lime.

CRUDE TAR.

SAMPLING.

Crude tar contains varying percentages of substances, such as water, ammoniacal liquor and free carbon, that have a tendency to stratify on standing. For this reason, special attention must be given the sampling. When shipments are made in bulk, a sample is readily taken by having a ¼" pipe tapped in the main. The pipe should extend to the center of the main, where it is bent at a right angle pointing in the direction of the flow of the tar. A small stream is thus allowed to flow continuously into the receiver throughout the delivery.

Tanks, barrels, etc., are sampled by means of a bottle attached to a long rod. The bottle is carefully lowered and raised from top to bottom of the liquid, at such a uniform rate that it is not quite filled when it reaches the surface. A sample can also be taken with a coring apparatus provided

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with a suitable valve at the lower end. When this apparatus is lowered to the bottom of the container, the valve will close, and a complete section of the tar can thus be removed.

In all cases, after the sample is taken, it is thoroughly mixed by stirring and poured immediately into wide-mouthed quart bottles or cans, before separation of water or carbon can take place.

SPECIFIC GRAVITY.

The Hubbard specific gravity bottle, special type, is recommended for this determination on account of the ease with which the tar can be introduced and removed. The tar sample is first dehydrated by heating to a temperature of 205° C. in a still such as is used for the determination of water hereinafter described. Any oil which is distilled over is carefully separated from the water, returned to the still and thoroughly mixed with the tar after it has sufficiently cooled. The specific gravity bottle previously calibrated with distilled water at 15.5° C. is filled to approximately two-thirds of its capacity with dehydrated tar and placed in hot water until air bubbles have disappeared. It is then cooled to 15.5° C. and weighed. The bottle is filled with freshly boiled distilled water and brought to 15.5° C., the water adjusted to the mark and weighed. The weight of tar divided by the weight of water displaced gives the specific gravity, e. g.:

a=weight of empty bottle.

b= " " bottle+water.

c= " " bottle+tar.

d= " " bottle+tar+water.

$$\text{Sp. Gr.} = \frac{c-a}{b+c-(a+d)}$$

WATER.

The still (see cut) used for this determination has a capacity of about one litre and a diameter and height of approximately 3½" and 6", respectively. It is made of heavy copper or cast iron with a turned ring at its upper edge. The lid, which is made of brass or iron, is fastened to the still by a single screw clamp which passes over the top. In order to make the joint between the lid and still gas tight, a cardboard, paper or asbestos gasket, covered with graphite to prevent sticking, is placed between the two metal surfaces. The condenser consists of a copper trough (for

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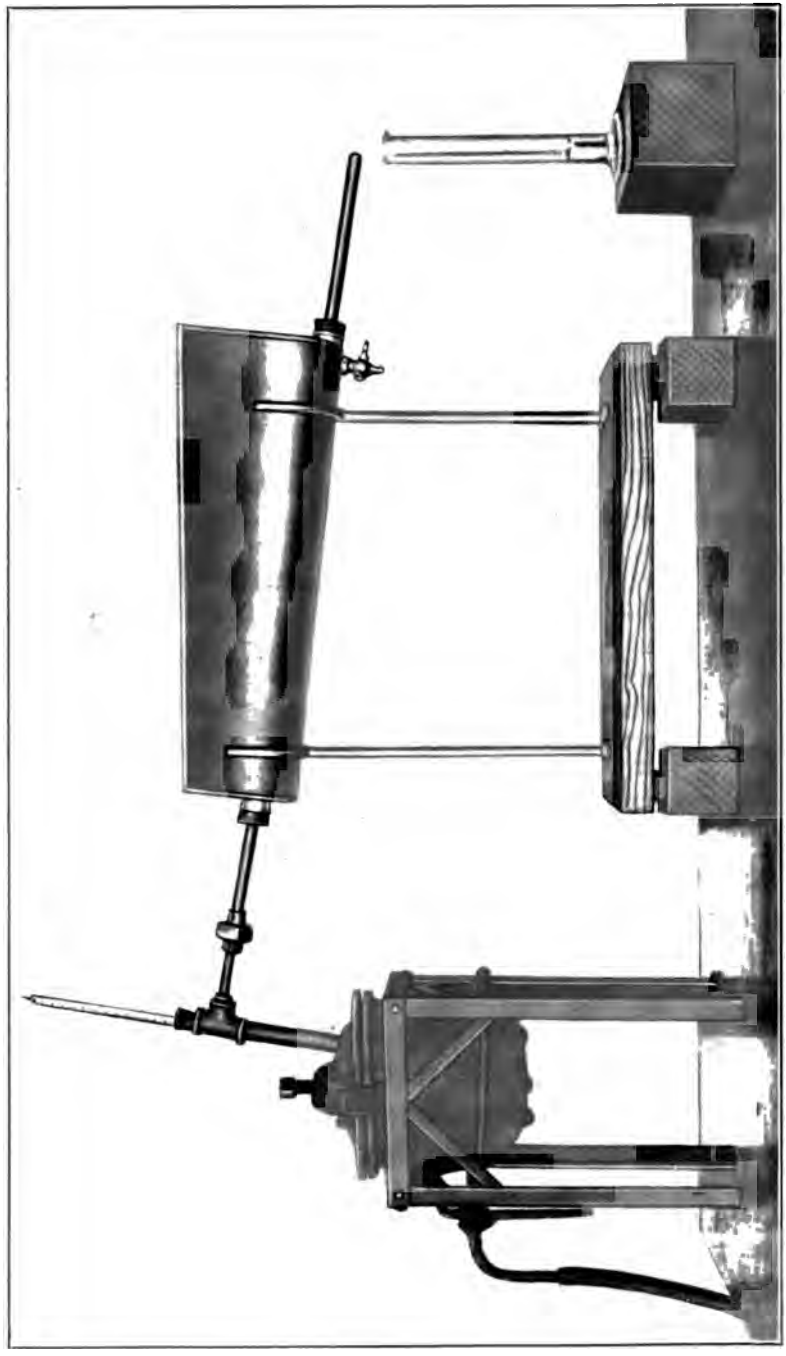

STILL AND CONDENSER FOR TAR DETERMINATIONS.

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description see Benzol Products) open at the top and through which passes a tube 22" in length and ½" in diameter. An ordinary distilling head connects the tube with the still. Both the distilling head and tube can be made of either metal (as shown in photograph) or of glass. If metal is used, it is tapped into the lid and connected with the tube by a metal union, using a cork gasket; if glass, both connections are made with cork stoppers. The thermometer is held in place by means of a perforated cork, and it is adjusted so that the top of the mercury bulb is just below the middle of side tube. The still is heated by a ring burner, and the distillate is collected in a 120 cc. graduated separatory funnel (special), to which 15—20 cc. of benzol has been previously added. Two hundred cc. of the sample, measured in a graduated cylinder, are transferred to the still. The cylinder is washed with 75—100 cc. light oil (freed by distillation from water) to remove the adhering tar, and the washings added to the still. The use of light oil, aside from insuring a full sample, has other advantages; the tar is thinned, the time required for the distillation reduced, and the water is completely carried over during the distillation, while the crystallization of naphthalene in the condenser tube and receiver is materially lessened. After the addition of the light oil washings to the still, the lid is clamped, the distilling head inserted and the condenser connected. The ring burner is first so placed that the flame will strike the jacket at the tar level. The burner is lowered from time to time, depending upon the flow of condensed oil. When the determination is almost completed, solid naphthalene may separate in the tube; this is melted by heating the water in the copper trough. The distillation is continued until the thermometer registers 205° C., when the volume of water is noted after rotating the funnel and allowing the contents to settle for a few minutes.

$$\%\ \text{of water (by volume)} = \frac{\text{No. of cc. water} \times 100}{\text{No. of cc. of sample used}}$$

FREE CARBON.

For this determination, two types of apparatus are recommended—the Barrett modification of the Underwriters' extractor, and the Wiley extractor. For either apparatus, the tar sample is first passed through a 30-mesh sieve and then dehydrated as described for the specific gravity determination.

Modified Underwriters' Extractor. Two to five grams of tar are weighed into a small beaker and digested with about 30 cc. of C. P. toluene on a steam bath. Two filter papers, No. 575 S. & S., the one 15 cm. and the other cut to 14 cm., are extracted, dried at 105° C., and weighed in a weighing

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bottle. They are then folded—the inner paper being the smaller one—around a rod (1.5 cm. diameter) so as to form a cylindrical cup. The papers are transferred to the wire basket, the supernatant liquid in the beaker is decanted through, the tar washed two or three times with hot toluene, and the residue then transferred to the cup. The beaker and contents are transferred to the flask containing C. P. benzene, and the extraction is continued by heating on a steam or water bath until the descending liquid is no longer colored. The papers are then dried and weighed in a weighing bottle. In order to prevent carbon from creeping over the paper cup during the final extraction, a filter paper cover may be placed over the residue in the cup.

$$\text{Free carbon} = \frac{\text{increase in weight of cup} \times 100}{\text{weight of tar}}$$

WILEY EXTRACTOR.

The crucible is fitted with double filter papers, filled with cotton, and the whole is extracted, dried and weighed in a weighing bottle. The sample is placed between layers of cotton and extracted with C. P. benzene on a steam or water bath, until the descending liquid is no longer colored. The crucible and contents are then dried and weighed, and the free carbon calculated as described in the preceding method.

VOLATILE MATTER AND FIXED CARBON.

Volatile matter and fixed carbon are determined as described under coal, except that the tar is gently heated for a few minutes until the tendency to foam is passed.

ASH.

Five grams of tar are transferred to a weighed porcelain or platinum crucible and ignited carefully until the carbonaceous matter is completely consumed.

$$\% \text{ ash} = \frac{\text{increase in weight of crucible} \times 100}{5}$$

VISCOSITY.

The Saybolt viscosimeter is used and time of flow of 60 cc. at 100° F. is taken.

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COMPLETE DISTILLATION OF TAR.

The distillation should be made on dehydrated tar. The same type of apparatus as is previously described under the determination of water, except a larger still 5½" x 7½" is used. The still is placed on the pan of a trip or prescription balance and weighed. Approximately 500 cc. of tar are transferred to the still, and the whole weighed. The distillation is conducted as for the determination of water up to 205° C., receiving the distillate in a graduated separatory funnel. If any measurable amount of water is present in the distillate, the distillation is stopped, the oil is separated and returned to the still as soon as the contents have cooled to room temperature. The distillation is started anew and carried without interruption to 350° C. The flow of oil is increased by placing a small Bunsen burner under the bottom of the still. The distillates are collected in weighed bottles, the following fractions being taken and reported as per cent. by weight:

0°—170° C.=Light Oils.

170°—230° C.=Carbolic Oils and Naphthalene.

230°—270° C.=Creosote Oils.

270°—350° C.=Anthracene Oils.

Residue=Pitch.

BENZOL PRODUCTS.

GENERAL REMARKS.

In the plant operation, benzol products are recovered from coke oven gas by scrubbing or washing the cooled gas with a high boiling point oil, known as "straw" or wash oil. The gas is forced upward through a series of scrubbers, meeting a fine spray of descending wash oil introduced at the top of the scrubber.

The "benzolized" wash oil from the final scrubber is preheated and passed through a separating still or column in which it is subjected to the action of super-heated steam which drives off the greater portion of the absorbed benzols. The de-benzolized oil from the separating still is cooled and used over again for the absorption of benzols. The benzol vapors, along with steam, pass from the separating still into a condenser where they are condensed to an oily liquid floating upon water, and constitute the crude "light oil."

Crude light oil contains many substances, principally benzene, toluene, xylenes, naphthas, naphthalene, carbon bisulphide, unsaturated hydro-carbons and a considerable amount of wash oil. The crude light oil is separated by

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fractional distillation into the various crude products, i. e., crude benzol, toluol, and light and heavy solvent naphtha. The residue consists mainly of wash oil and naphthalene. These crude products are agitated or washed with strong sulphuric acid and then with a solution of caustic soda and further rectified, thus producing refined and pure products.

The principal refined products are as follows: Water white benzol (refined first runnings), 90% benzol, commercial toluol (90% toluol), pure benzol and toluol, and refined light and heavy solvent naphtha (the latter seldom being refined). Refined products expressed in percentages refer not to the percentage of purity of the product, but to the amount coming over up to a definite temperature in the prescribed distillation test, e. g., 90% benzol; in the distillation test, 90% by volume will come over up to 100° C.

The principal tests are distillation tests. While these methods of testing are not strictly scientific, yet when properly conducted meet both the works and the trade requirements.

In the testing of benzol products, it is essential that the distillation apparatus be as uniform as possible, and the details of manipulation be strictly followed. The capacity of the distillation flask, diameter and length of neck, position and diameter of side tube, diameter and inclination of condensing tube, position of thermometer, size of hole in asbestos board and the rapidity of distillation are factors that enter into the securing of concordant results. The standard apparatus to be used is shown in photograph.

The distillation flask is round bottom of approximately 200 cc. capacity, diameter of flask 3″, length of neck 4″, diameter of neck ⅞″, position of side tube, center of neck, diameter of side tube ¼″, length of side tube 3″. The flask rests upon an asbestos board 6″ x 6″ x ¼″, having a hole in the center not greater than 1″ in diameter for testing pure products; the hole can be larger for crude products. The asbestos board is supported by a ring stand and heat is supplied by a Bunsen burner adjusted so as to give the proper rate of distillation. In order to protect the flame from air currents, the lower portion of the flask and the burner are enclosed on three sides by a box 7″ x 10″ x 14″, as shown in the print. However, it is pointed out that it may be advantageous to eliminate the portion of the box surrounding the flask; for, unless the proper precautions are taken, there is a possibility of super-heating the vapors in the distillation flask. A suitable cylindrical mica chimney (2½″ diameter), which protects the flame only, may be used.

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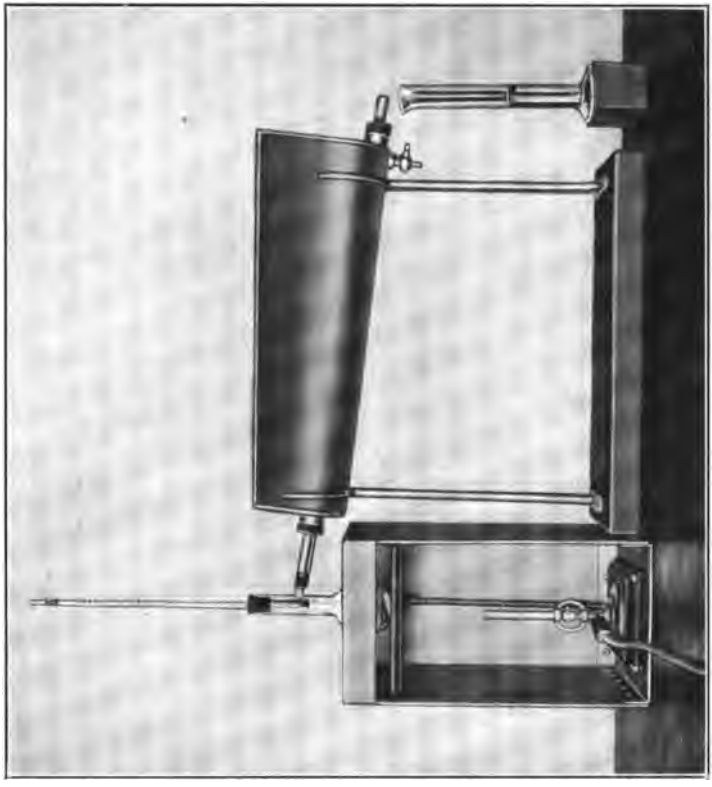

APPARATUS FOR BENZOL DISTILLATION TESTS.

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The thermometers used are different kinds, depending upon the products to be tested, and the operator should ascertain the accuracy of each one before using. The thermometers are held in position by means of a perforated cork stopper and so adjusted that the top of the bulb is just below the middle of the side tube. A copper condenser with round bottom of the trough type is used, being 18″ in length and 6″ in diameter. The height at one end is 4″, at the other 6″. The condenser tube is of thin glass, 22″ long, ½″ in diameter, and is held in place by rubber stoppers. The slope of the tube is slightly greater than that of the condenser trough, the hole at the upper end being 1″ higher than at the lower end. The trough is supported by two legs 15″ apart, the length of one is 12″, the other 10½″. The condenser is supported on a wooden block.

The *thermometers* used in the distillation tests should be both accurate and sensitive, and for light oils, crude benzols and naphthas, be graduated from 0—250° C. in 1° C. For the refined and pure benzene and toluene, thermometers graduated from 60—140° C. in 1/5ths are very satisfactory. In the use of thermometers graduated to 1/5° it is assumed that the operator will read to 1/10° if necessary. They should be selected with the view of always using for the same work thermometers of the same type, size, length and scaled for the same length immersion.

Before being put into use, the thermometers should be compared with standards and the corrections established. Standard thermometers having the following ranges of scale: 79—82° C.; 99—101° C.; 109—112° C., and 136—142° C., certified by the U. S. Bureau of Standards, are recommended. The thermometers for testing the refined and pure products should be compared with the standard at the boiling point of each product and distilled water, all at the standard barometric pressure. For the boiling point test, quantities of the pure products, showing a distillation range of about 1° C., are taken and fractioned through an efficient column, and the fractions with .2° C. range collected for use. In determining the boiling points a correction of .043° C. for benzene; .047° C. for toluene; .052° C. for xylene, and .037° C. for distilled water, is made for each mm. variation in barometric pressure from the standard 760 mm. at 0° C. The thermometers should be numbered, and the corrections necessary at the definite points noted. They should also be compared for sensitiveness at the first drop by the distillation of products having a range of about 2° C.

For the *determination of the boiling points* or comparison of thermometers, a suitable boiling point apparatus may be used, such as the Beckmann or Edwards.

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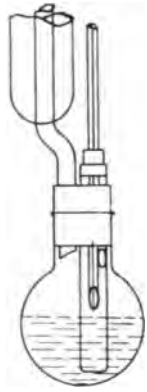
The Edwards apparatus illustrated (see cut) consists of a wide-mouth flask fitted with a cork carrying a reflux condenser and a short length of ½" diameter glass tubing, reaching to a point just clear of the bottom of the flask. A thermometer is inserted in the tube so that its bulb is ¼ of an inch from the surface of the liquid. A hole is blown in the tube, just below the bottom of the cork, to allow the vapor to circulate. The capacity of the bulb should be such that the liquid fills about one-half of it; 50 to 120 cc. is a suitable volume. The liquid is caused to boil up the tube and over the bulb of the thermometer until the temperature is constant. The flame is then shifted slightly to one side so that the ebullition takes place outside the tube, the temperature again being read when constant. This temperature is corrected for the barometric pressure.



EDWARDS' BOILING POINT APPARATUS.

TESTING OF LIGHT OIL AND BENZOL.

SAMPLING.

Tank cars or storage tanks are sampled by forcing a one-quart, cork stoppered bottle, with string attached to the cork, to the bottom of the car. The cork is then pulled and the bottle evenly and rapidly drawn from the tank so that it is not quite filled. About one gallon samples are taken.

The sampling outfit consists of a ¼" pipe long enough to reach to the bottom of the car, bent at one end to form a handle, and the other end is capped. Two laboratory rings are used to fasten the bottle to the pipe, one about 4" diameter being clamped near the end of the pipe to support the bottom of the bottle, the other, about 2½" diameter, is slipped over the neck and clamped securely. This holds the bottle firmly in place and is easily handled.

Small tanks and drums are sampled by means of a pipette, about ½" diameter, constricted at one end. This is lowered to the bottom of the drum and a sectional sample taken.

LIGHT OIL.

SPECIFIC GRAVITY.

For this and the distillation test, if containing more than one per cent. water, the oil must be dehydrated as described under Tar. The specific

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gravity is taken with a standardized hydrometer at 15.5° C., or at least 3° C., above the limpid point. A correction of .0008, for each degree above 15.5° C., is added to the specific gravity.

DISTILLATION.

For the distillation test, 100 cc. of oil are measured in a cylinder graduated to 1 cc. and transferred to a clean and dry standard distillation flask. The same measuring cylinder is used as a receiver for the distillate. A thermometer recording above 200° C. is inserted so that the top of the bulb is just below the middle of the side tube, and heat applied. The Bunsen flame is regulated to distill as rapidly as possible in distinct drops, or at the rate of about two drops per second. The temperature, when the first drop falls from condenser, is noted, and thereafter the cc. distilled at every even 10° C. up to 200° C., at which point the distillation is stopped. The residue above 200° C. in the flask is carefully drained into the cylinder and the loss noted.

In all benzol distillation tests there is always a small portion of the vapors that are not condensed. This amount, known as the "loss," is added to the volume at the different points. Thus, in the distillation of crude oil, the volume condensed at 200° C.,+"loss," is considered light oil.

CRUDE BENZOLS.

If sample contains sufficient water to produce turbidity, it is removed by filtering through dry filter paper.

SPECIFIC GRAVITY.

Hydrometer. The calibrations on the hydrometer should be based on water as 1 at 15.5° C., and the scale divided to the third decimal place. The specific gravity determination is made at a temperature of 15.5° C.

Westphal Balance. The instrument should be balanced in air, and calibrated with water as 1 at 15.5° C. The determination is made at the same temperature.

Pycnometer Bottle. The pycnometer should be calibrated with water at 15.5° C., and the determination made at the same temperature.

DISTILLATION.

Conducted as for light oil, but carried to dryness, and the temperature at first drop and 5 cc., and volumes condensed at each even 5° C. thereafter, and the dry point noted. When the last drop of oil is vaporized, the flame is instantly removed in order to avoid superheating of the vapors.

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TOTAL SULPHUR.

The method consists of vaporizing the benzol in a flask with a stream of air, burning the benzol-air mixture at a capillary tip, and absorbing and subsequently determining the generated sulphur dioxide. The benzol is vaporized in a 50 cc. round bottom Florence flask, which is closed with a 2-hole rubber stopper provided with a long right angle tube extending to the bottom of the flask, and a short right angle tube which serves as the exit for the benzol-air mixture.

Approximately 10 grams of the sample are transferred to the flask, the stopper is inserted, and the whole transferred to a water bath maintained at a temperature of 30 to 40° C. The long right angle tube is connected by rubber tubing to a compressed air line and the short tube to a capillary tip. A stream of air is then passed through the flask and the gas mixture ignited at the tip. Toward the end of the test, the temperature of the water bath is raised to 75° C. in order to volatilize completely the sulphur compounds of higher boiling points.

The products of combustion may either be passed through the Referee's apparatus and the sulphur subsequently determined by this method, or they may be sucked through three absorption bottles containing hydrogen peroxide, whereby the sulphur dioxide is oxidized to sulphur trioxide. In the latter case the sulphur may be determined gravimetrically, or the sulphuric acid may be titrated with N/10 caustic soda solution, after expelling the hydrogen peroxide by boiling.

The time required for the determination is from 5 to 6 hours. There is no danger of explosion by striking back of the flame, and the proportions of the gas mixture can be so regulated that no soot will be formed by incomplete combustion.

REFINED BENZOLS.

Same as for crude.

PURE PRODUCTS.

Same as for crude, noting the temperatures at first drop, 5 cc., 95 cc. and dry.

In all benzol distillation tests, the boiling point is materially affected by the barometric pressure. The barometer should be read at time of distillation and the temperature correction for variations from standard pressure accordingly added or subtracted for the specified points.

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ACID WASHING TEST.

The set of color standards consists of 15 bottles (French squares, flint glass, glass-stoppered, one ounce capacity), each containing one of the colored solutions made up as given below and the bottle sealed with paraffin.

When making a test for amount of acid washing, a similar bottle is used. Seven cc. of C. P. sulphuric acid (1.835—1.84—sp. gr.) are placed in the bottle, followed by approximately 21 cc. of the material to be tested. The contents of the bottle are shaken thoroughly for 15 to 20 seconds, and allowed to stand for the specified time. The resulting color of the acid layer is compared with the standard set to determine its corresponding number. If the mixture of the oil and acid is not sufficiently shaken, a dark ring may form between the layers, after standing for 15 minutes. In such a case, the bottle is slightly shaken so as to have a uniform color before comparing with the standard,

In pure benzol and pure toluol testing, the benzol or toluol layer must remain white, and the color of the acid layer, after standing 15 minutes, must not be darker than No. 4.

For 90% benzol and all grades of benzol and toluol other than pure, the benzol and toluol layer must remain white, and the color of the acid layer, after standing 15 minutes, must not be darker than No. 6.

For solvent naphtha, the acid layer color only is noted, and after 5 minutes' standing it must not be darker than No. 14.

It is well to note that the above schedule shows the limit of color allowable in the sales specifications; and it is to be expected that to consistently pass the test, Works' practice should call for a limit of at least one number lighter in each case.

The solutions for the standards are made up as follows:

The following basic solutions are used:

A—59.4965 gr. $CoCl_2.6H_2O$ (nickel free) is made up to 1000 cc. with a mixture of 25 cc., 31% HCl and 975 cc. H_2O.

B—45.054 gr. $FeCl_3.6H_2O$ made up to 1000 cc. with a mixture of 25 cc., 31% HCl and 975 cc. H_2O.

C—3.5 volumes of Solution A+36.5 volumes Solution B+90 volumes of H_2O.

D—3.5 volumes of Solution A. 36.5 volumes of Solution B. (No water is added.)

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E—Solution of K_2CrO_4 saturated at 21° C.

F—One volume of a solution of $K_2Cr_2O_7$ saturated at 21° C. One volume of H_2O.

As standard color solutions to be used for comparison, the following are made up and numbered from 0 to 14:—

No. 0—Pure Water.

No. 1—One volume of Solution C. 1 volume of H_2O.

No. 2—5½ volumes of Solution C. 2 volumes of H_2O.

No. 3—Solution C as such.

No. 4—One volume of Solution D. 1 volume of H_2O.

No. 5—5½ volumes of Solution D. 2 volumes of H_2O.

No. 6—Solution D as such.

No. 7—5 volumes of Solution E. 2 volumes of H_2O.

No. 8—Solution E as such.

No. 9—7 volumes of Solution E. ½ volume of Solution F.

No. 10—6½ volumes of Solution E. 1 volume of Solution F.

No. 11—5½ volumes of Solution E. 2 volumes of Solution F.

No. 12—One volume of Solution E. 1 volume of Solution F.

No. 13—Two volumes of Solution E. 5 volumes of Solution F.

No. 14—Solution F as such.

DETERMINATION OF BENZOL IN GAS.

The apparatus consists of a series of seven 2½ litre bottles connected for gas washing by means of ¼" glass tubing through two-hole rubber stoppers, short rubber connections, and to an accurate gas meter. The first bottle is wide mouthed and has ½" glass tube connecting with gas supply and extending nearly to the bottom of the bottle. The bottle is used empty as a drip bottle. About one litre of paraffin oil is placed in each of the remaining six bottles, the gas inlet tubes adjusted so that the ends dip about 1½" below the surface of the oil. The end of the gas inlet tube may be provided with several small openings in order to divide the gas entering the oil into several small streams. The absorption train is placed in a large container so that the bottles can be kept surrounded with water at about 20° C. The gas is passed at the rate

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of 3 to 4 cu. ft. per hour. For a determination of the unwashed gas at least 75 cu. ft. of the gas are used, and 250 cu. ft. for washed gas.

The apparatus requires some attention from time to time throughout the period of test. and the gas volume is reduced to standard conditions from the average of observations of temperature and pressure (see U. S. Steel Corporation Gas Pamphlet). The oil is transferred to a suitable apparatus, constructed of either copper or iron, of about three gallons capacity (see cut) and steam distilled. (In making daily determinations, the still should be examined frequently for leaks.) It is pointed out that it is optional with the operator whether the oil is steam distilled directly or first heated to 100° C. before distilling, as experiments made appear to indicate that the same results will be obtained by either procedure. The still containing the oil is connected with a 36" Liebig condenser having a glass or copper condensing tube, and to a small generator heated by a Bunsen burner which supplies steam under pressure. The heat is regulated under the generator so that about 1½ hours are required to condense one litre of water. The distillate is received in an oil trap in which the oil and water separate, and the latter is drawn off continuously from the bottom of the trap into a measuring flask. When one litre of water has been condensed the distillation is stopped, the oil separated from the water and distilled up to 200° C. as under light oil.

The correction for loss is determined by a blank test made under the same conditions, and using approximately the same amount of light oil previously distilled up to 200° C. This blank test is very necessary for the reason that benzols are not entirely insoluble in water, and to take care of the loss from vaporization and other causes.

The residue in the flask above 200° C. is transferred to a copper beaker and cooled to 15.5° C. After being maintained at this temperature for 15 minutes, the mass is filtered through paper placed in a Hirsch funnel, sucked dry and pressed between filter papers in a letter press and weighed as naphthalene.

DETERMINATION OF BENZOL IN BENZOLIZED AND DEBENZOLIZED OIL.

An average drip sample of these oils for twenty-four hours is taken from the lines. It is steam distilled and the oil fractioned as described under Benzol in Gas. The blank is made by using light oil up to 200° C., recovered from the debenzolized oil.

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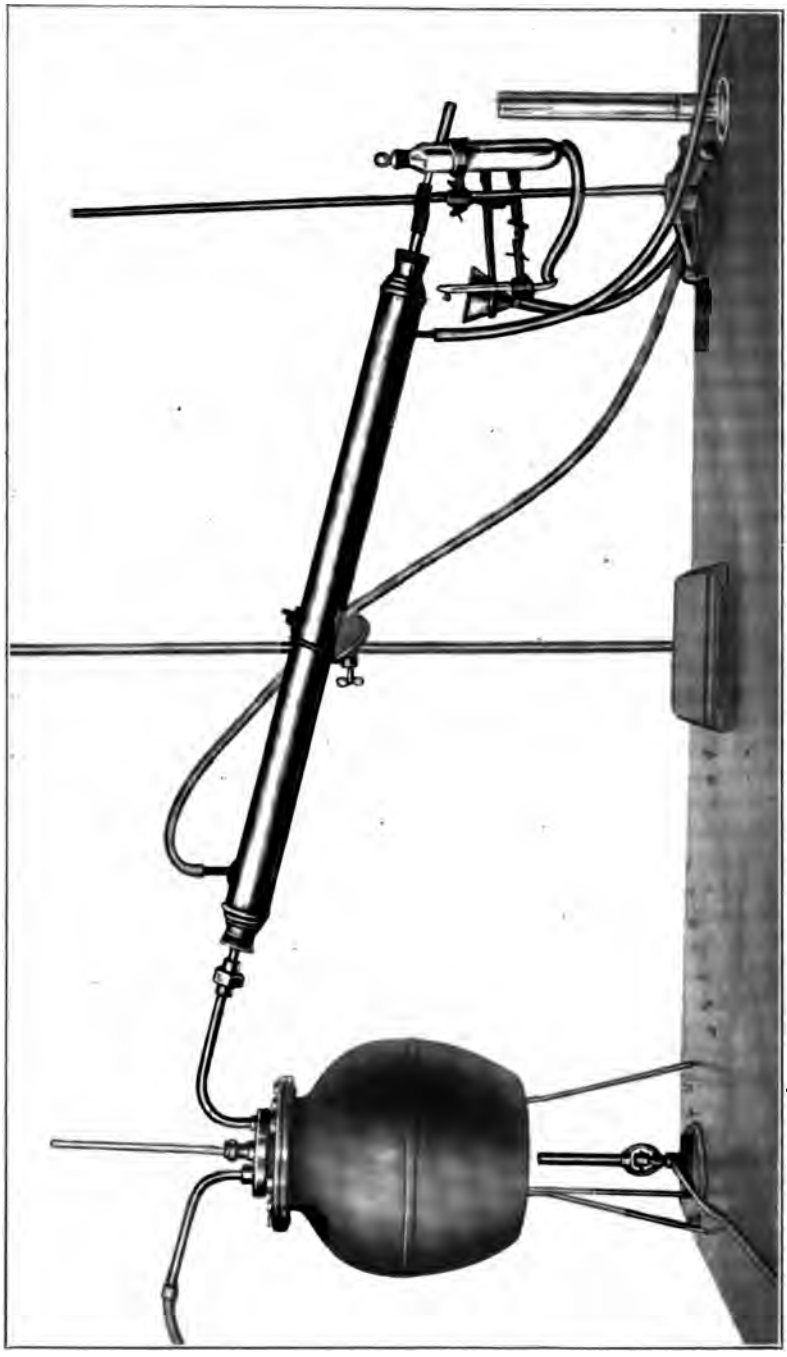

APPARATUS FOR WASH OIL DISTILLATION TESTS.

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PHYSICAL TESTS OF WASH OILS.

In order to insure a uniform quality of wash oil, the following physical tests are made:

SPECIFIC GRAVITY. This is determined at 60° F. by means of a hydrometer or a Westphal balance.

FLASH AND FIRE POINT. The open cup method is used, the oil being heated so that the temperature rises 10° F. per minute. A flame ¼" long is passed over the oil ¼" above the surface after each 5° rise in temperature. The point at which a flash is first obtained is reported as the "flash point," and the point at which the oil burns continuously is called the "fire point."

VISCOSITY. The Saybolt standard viscosimeter is used. The test is made at 100° F. by noting the time required for 60 cc. to pass through the aperture.

CLOUD TEST. This test is made by placing 1" of oil in a ground glass stoppered bottle of 1" diameter. The oil is cooled at the rate of 1° F. per minute, stirred constantly with a thermometer and the temperature noted when a faint cloud appears in the oil.

FRACTIONAL DISTILLATION. This is made in the same manner as with a benzol or light oil, noting the temperature at the start and the amount off at each 18° F. until 95% is off.

The following are typical specifications for wash oil:

Specific Gravity	35 to 35.5 Baume.	
Flash Point	285° F.	
Fire Point	345° F.	
Viscosity	45 to 50 at 100° F.	
Cloud Test	28	
Distillation Test	536°—554° F.	1%
	572° F.	5%
	590° F.	11%
	608° F.	13%
	626° F.	18%
	644° F.	17%
	662° F.	9%
	680° F.	8%
	698° F.	6%
	716° F.	4%
	734° F.	1%
	752° F.	2%
	768° F.	2%

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LABORATORY METHOD FOR DETERMINING THE RELATIVE YIELDS OF COKE AND BY-PRODUCTS IN BITUMINOUS COAL BY THE PROGRESSIVE DRY DISTILLATION PROCESS.

The results obtained by this method of determining coke, gas and by-product yields from coal are naturally somewhat relative, since it is practically impossible to conduct these tests in the laboratory under the conditions of time, temperature and mass occurring in the regular coke plant operation.

By frequent comparison of laboratory results from time to time with those obtained in actual practice, a valuable correlation between laboratory and actual results is obtained, and a good theoretical estimate of the coke, gas and by-product yields of any given coal can be secured.

When conducting tests by this method, care must be taken to maintain, at all times, similar laboratory conditions with the strictest regard to the observance of time and temperature factors.

PREPARING THE COMBUSTION TUBE.

The sample of coal used for analysis is crushed to pass a 40-mesh sieve and dried at 105° C. This size coal has given the best results, as a sample pulverized finer is apt to evolve its volatile matter so rapidly that it cannot be taken care of by the absorption train. The distillation is made in a Jena glass combustion tube, closed at one end; length 20″; outside diameter $\frac{13}{16}$″; thickness of wall, approximately $\frac{3}{32}$″. The tube is charged in the following manner (see cut):

Twenty grams of coal are transferred to the tube by means of a glass funnel. An asbestos plug, rolled up in the hand to a thickness of ½″, is loosely placed in the tube 11½″ from the closed end; a ¼″ air space is left and another ½″ asbestos plug inserted. The next 3″ of the tube are filled with dried silica brick, crushed to pass a 10 and held on a 20-mesh sieve, and another ½″ asbestos plug inserted to hold the brick in place. The purpose of the silica brick is to have conditions in the tube for the gases similar to those in a coke oven. The placing of the plugs at the above measurements leaves a space at the open end of the tube 3¾″ long, which, hereafter is known in the distillation as the tar-piece or cut-off end. The tube thus prepared is weighed.

The tar-filter (see print) is prepared by packing the entire middle section and but one-half the large end of the filter tube with dried absorbent cotton

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to remove the suspended tar. The tar-filter thus prepared is weighed and connected to the open end of the combustion tube by a strong, air tight cork.

SETTING UP ABSORPTION TRAIN.

Eight to ten cc. of normal sulphuric acid, depending on the ammonia content of the coal, are placed in the first Liebig bulb and two drops of methyl orange are added as an indicator. In this bulb, the evolved ammonia naphthalene and water from the coal are absorbed and the ammonia subsequently determined by titration with N/10 sodium carbonate.

In the second Liebig bulb about 13 cc. of a solution of potassium hydroxide (1-1) are placed to collect the carbon dioxide and the hydrogen sulphide formed during distillation.

The third and fourth Liebig bulbs are each filled with about 13 cc. of liquid paraffin oil to absorb the evolved benzol. Each of the four Liebig bulbs is now weighed with an accompanying calcium chloride "U" tube.

The coal in the combustion tube is leveled by slight tappings so as to give a free and open passage for evolved gases. The weighed charged tube is then placed on an asbestos-covered iron or clay trough in the combustion furnace. The tar filter, having been inserted through the openings in the copper boiler serving as a steam bath, is connected to the combustion tube. The first Liebig bulb, containing the sulphuric acid, is now connected to the small end of the tar filter by good seamless rubber tubing. The remaining three bulbs, with their respective calcium chloride tubes, are then connected after the sulphuric acid bulb and calcium chloride "U" tube as shown in the cut. The absorption bulbs are placed in small battery jars. For the collection of the purified gas, a gasometer of 12 litres capacity, graduated to 200 cc., having a large 4-holed rubber stopper for gas-inlet, manometer, thermometer and syphon to a lower receiver, is connected to the last calcium chloride "U" tube.

APPLICATION OF HEAT.

The train is now tested for leaks by opening all the stop-cocks and lowering the leveling bottle to produce suction from the gasometer. If no air is entering from without, the air bubbles passing in the train will soon cease. The rubber connections are wired, if necessary. When the train is found to be air tight, the first four burners of the combustion furnace and the burner under the steam bath are lighted. The first four burners of the furnace heat the silica brick in the tube.

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After the silica brick becomes heated to a cherry red color, the gas entry stop-cock on the gasometer is closed and the gasometer refilled with water, leaving it shut off until the first burner under the coal, which is lighted immediately, has distilled off enough gas to prevent the water in the gasometer from being drawn back into the train. The stop-cock on the gasometer is then opened and the collection of the gas begun. After a few minutes, the pressure has increased enough in the train so that ice and water can be safely placed around each Liebig bulb.

It is best to keep all absorbing bulbs, especially the first, in ice water, to cool the gases passing through the train so as to get the most efficient absorption. The burners under the coal are regulated so that the inner cone of the flame touches the trough in which the combustion tube rests. Burners are then lighted approximately every ten minutes, in their respective order, regulating the time by the velocity at which the gas comes over. After all burners are lighted, heating is continued until the gas passing through the train amounts to about five bubbles per minute. The stop-cocks on the gasometer and on the train are now closed and the distillation is stopped. The total time of distillation varies from 2 hours 10 minutes to 2 hours 30 minutes, according to the quantity of gas evolved from the coal under examination. Frequent temperature readings are taken during the process of distillation by placing a thermo couple on the tube. Nine hundred degrees C. should be reached, even if it is necessary to set up a blower in the gas line to increase the pressure.

DISCONNECTING THE TRAIN AND SUBSEQUENT MANIPULATION.

The apparatus is allowed to cool somewhat, and the absorption train is disconnected from the tar filter and gasometer. Air, free from carbon dioxide and moisture, is slowly drawn through each Liebig bulb and "U" tube for approximately 45 seconds to displace the gas; the bulbs are then wiped dry and allowed to assume balance temperature before weighing.

The tube and tar filter, when sufficiently cool, are weighed. The part of the combustion tube in which there is an accumulation of tar and tarry oils is cut off and weighed, after which this cut-off end, together with the cotton in the tar filter, is boiled with water for 10 minutes for the extraction of combined ammonia which is present with the tar. The tar is then burned off the cut-off end and the end re-weighed.

The first bulb contains the free ammonia absorbed in the sulphuric acid, naphthalene and the water derived from the combustion of hydrogen and oxygen

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occurring in the coal. After the removal of naphthalene, the contents of the bulb are transferred to a litre Florence flask and the acid titrated with N/10 sodium carbonate. This first titration is made to give an idea of the ammonia content, so as to gage the amount of N/10 sulphuric acid required for absorption on distillation, which is conducted as follows:

Twenty cc. of strong potassium hydroxide solution (1-1) are added to the solution in the flask and the contents distilled into a sufficient quantity of N/10 sulphuric acid (usually 50 cc.). It is advisable to make a blank on potassium hydroxide and water used, making corrections in each case as found.

To determine the combined ammonia, the boiled washings from the tar filter and cut-off end are transferred to a distilling flask, diluted with water to about 200 cc., strong potassium hydroxide solution (1-1) added, and distilled into a sufficient quantity of N/10 sulphuric acid, usually 10 or 15 cc.

The naphthalene retained by the sulphuric acid bulb is collected on a weighed filter paper, then washed with cold water, dried in a desiccator and weighed. The quantity of naphthalene increases with the temperature of distillation. This determination is not often made.

CALCULATIONS.

Grams Volatile Matter equals the difference in the weight of the combustion tube before and after the distillation, plus the weight of the tar found in the tar piece.

Grams Coke equals the grams volatile matter subtracted from twenty.

Grams Tar equals the sum of the increase in weight of the tar filter plus the naphthalene, plus tar found in tar piece, minus grams combined ammonia.

Grams Water equals the increase in weight of the sulphuric acid bulb minus the naphthalene and the grams of free ammonia.

Grams Hydrogen Sulphide are determined by diluting the contents of potassium hydroxide bulb up to 100 cc. and titrating 10—25 cc. portions with N/10 iodine solution, after which it is calculated to grams hydrogen sulphide.

Grams Carbon Dioxide equals the increase in weight of the potassium hydroxide bulb, minus the grams hydrogen sulphide.

Grams Free Ammonia equals the cc. N/10 sulphuric acid used, multiplied by 0.0017.

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Grams Combined Ammonia equals the cc. N/10 sulphuric acid used, multiplied by 0.0017.

Grams Crude Benzol equals the sum of the increases in weight of the two paraffin bulbs.

Grams Sulphur in the gas equals the cc. N/10 iodine solution used in titrating hydrogen sulphide, multiplied by 0.0016.

Grams Gas equals the grams volatile matter—(tar+ammonia+naphthalene+water+carbon dioxide+hydrogen sulphide+benzol).

To find the percentage of each constituent, the result in grams is multiplied by 5.

GAS CALCULATIONS.

After noting the volume and temperature of the gas in the gasometer, a sample is withdrawn and analyzed according to the standard methods as given in the U. S. Steel Corporation gas pamphlet. Any free oxygen found in the gas from a coal distillation is caused by leaks or by the air which could not be drawn from the train before combustion was started. Now, since air is four-fifths nitrogen, four times the oxygen volume found is subtracted from the nitrogen as due to nitrogen in the air, and five times the volume is added to the hydrogen.

This method of calculating the hydrogen content of gas has been adopted after proving by experiments, that the gas left in the train at the end of the combustion consists almost wholly of hydrogen.

THERMAL VALUE OF THE GAS.

Having the composition of the gas, its total heat value will equal the sum of the products obtained by multiplying the percentage by volume of each constituent gas by its thermal value as given in the United States Steel Corporation gas pamphlet.

$$\text{B. t. u. value of gas per pound of coal} = \frac{\text{cu. ft gas (62° F., 30″ mercury) net ton dry coal} \times \text{B. t. u. per cu. ft. of gas.}}{2000}$$

SPECIFIC GRAVITY OF THE GAS.

The specific gravity of the gas can be obtained by the following methods of calculation, the first of which is preferable:

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(a) By adding the products obtained by multiplying the percentage by volume, of each constituent gas by its specific gravity.

(b) From the results of the distillation by dividing the grams of gas by litres of dry gas at 62° F. and 30″ mercury, and then dividing this result by 1.221, (the weight of one litre of air at 62° F. and 30″ mercury).

CALCULATIONS FOR REDUCTION OF OBSERVED VOLUME OF GAS TO STANDARD CONDITIONS.

The observed volume of gas is reduced to standard conditions, dry gas at 62° F. and 30″ mercury, and wet gas at 62° F. and 30″ mercury, by use of standard corrections for tension of aqueous vapor (see U. S. Steel Corporation gas pamphlet). For dry gas the tension of aqueous vapor at the observed temperature is subtracted from the observed pressure, and the volume corrected to 62° F. and 30″ mercury by the use of the factor as given in the gas pamphlet. For wet gas the tension of aqueous vapor at 62° F. is added to the standard pressure, 30″ mercury and the gas volume corrected again by the use of the factor to 30″ mercury.

CALCULATION FOR DETERMINATION OF VOLUME OF HYDROGEN SULPHIDE.

The volume of hydrogen sulphide is calculated from its weight by dividing the latter by 1.442 (the weight of one litre of hydrogen sulphide at 62° F. and 30″ mercury).

CALCULATION FOR DETERMINATION OF VOLUME OF CARBON DIOXIDE.

The volume of carbon dioxide is calculated from its weight by dividing the latter by 1.867 (the weight of one litre of carbon dioxide at 62° F. and 30″ mercury).

REPORTING PER CENT. PRACTICAL YIELDS.

Per Cent. Coke. In correlating the laboratory and practical yields, it has been found necessary to make the following allowances on the laboratory values when reporting the per cent. practical yields. From the per cent. coke obtained in the tube, one and one-half per cent. is subtracted and the resulting figure taken as the practical coke yield.

Per Cent. Tar. Of the tar found in the volatile matter, 106% is reported as the practical yield.

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Per Cent. Ammonium Sulphate. The per cent. ammonium sulphate is found by multiplying the percentage of total ammonia content by factor 3.88. Ninety-four per cent. of the theoretical yield is reported as the practical yield.

Per Cent. Benzol. This value is reported 100%, or as obtained, without any additions or deductions.

Cubic Feet of Gas.

The cubic feet of gas per net ton of coal may be reported as follows:

1—Dry gas at 62° F. and 30″ mercury.

2—Wet " " 62° F. " 30″ "

3— " " " 62° F. " 30″ " +carbon dioxide and hydrogen sulphide.

The cubic feet per net ton of coal are found by multiplying the observed volume in litres of gas by the factor 1600. The cubic feet of carbon dioxide and hydrogen sulphide per net ton of coal are found by multiplying the calculated volume in litres of gas by 1600.

The factor 1600 is the ratio between litres of gas on a basis of 20 grams to cubic feet per net ton of coal as is shown by the following calculation:

1 litre=.0353 cu. ft.

1 ton (net)=907200 grams.

$$\frac{.0353 \times 907200}{20} = 1601 \text{ or } 1600, \text{ as used in practical work.}$$

REPORTING EQUIVALENTS PER NET TON OF COAL.

Pounds Ammonium Sulphate. This figure is found by converting the per cent. practical yield to pounds per net ton of coal.

Pounds Crude Benzol. The percentage of crude benzol found in the volatile matter of the coal is calculated to pounds or gallons per net ton of coal. The gallons of benzol are found by dividing the pounds of benzol by 7.34 (assuming sp. gr. of crude benzol as .88).

Gallons Tar. This figure is found by converting percentage of tar found in per cent. practical yield to gallons per net ton of coal. To obtain this

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figure, the percentage of tar reported as practical yield is multiplied by 2, as is shown by the following calculation:

Let x=percentage of tar as practical yield,

$\frac{2000x}{100}$ or 20x=pounds tar per 2000 pounds of coal,

Sp. Gr. of Tar=1.20,

1 Gal. Water=8.34 pounds,

Therefore, 1 gallon of Tar=10.00 pounds.

Then $\frac{20x}{10}$ or 2x=gallons tar per net ton of coal.

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